Heterocyclic Carbonium Ions -- Free and Complexed

By

PETER WILLIAM WENTZ

A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA
1972

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the people who have made this work possible as well as the professional associations and personal friendships involved. Listed in alphabetical order:

Dr. Kenneth Abbate
Dr. Merle Battiste
Dr. B. C. Bhattacharyya
Joe Drueke
Mrs. Mary Geiger
Jim Horvath
Marty and Sharon Kulig
Dr. Kenneth McKerns
Bruce McMaster
Bud Mihal
Dr. George Ryschkewitsch
Barry Sanderson
Dr. R. Carl Stoufer
Joe Strouse
Joe Vaughn
Dr. J. Kenneth Watson
Neil Weinstein
Stan Weller
Dr. William Weltner
Mr. and Mrs. Charles Wentz

A special tribute to my loving wife Margie is long overdue. She is a comfort in times of fear, anger, frustration, and bitterness and a joy in times of love, peace, and happiness. Her faith, determination, and strength make anything possible.

TABLE OF CONTENTS

TABLE OF CONTENTS -- Continued

LIST OF TABLES

LIST OF FIGURES

Abstract of Dissertation Presented to the Graduate Council of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

HETEROCYCLIC CARBONIUM IONS -- FREE AND COMPLEXED

By
Peter William Wentz
June, 1972

Chairman: R. Carl Stoufer
Major Department: Chemistry

The syntheses of several series of thiazolyldiphenylmethanols is reported. The thiazolyl moieties include 2-thiazolyl, 4-methyl-2-thiazolyl, 4,5-dimethyl-2-thiazolyl, and 2,4-dimethyl-5-thiazolyl with the phenyl rings substituted at the _para_-position by -H, $-CH_3$, and $-OCH_3$. Protonation of the thiazole ring nitrogen in acidic media precedes carbonium ion formation which occurs at relatively high acid strengths. The relative stabilities of these di-positive cations HR^{+2} were determined by measuring their relative electrophilicities toward water for which the species in equilibrium are HR^{+2} and $HROH^{+1}$. These thermodynamic stabilities were determined by employing the H_R acidity function shown to be appropriate for these systems. Within a particular series the stability increases as the phenyl _para_-substituent changes from -H to $-CH_3$ to $-OCH_3$ as

expected. Methyl substitution at the 4- and 5- positions of the thiazole ring was found to enhance the stability of the carbonium ion also. Members of the 2,4-dimethyl-5-thiazolyl series are the most stable among those with identical phenyl substituents, a fact attributed to the greater number of bonds and the greater distance separating the centers of positive charge.

The preparation of the 1:2 dichloropalladium(II) complexes of the thiazolyldiphenylmethanols preceded the generation of the corresponding complexed carbonium ions in perchloric acid. The complexed cations are more stable than their free carbonium ion analogues. In the only system investigated an increase in the stability of the complexed cation was observed when the coordinated chloride ions were replaced by bromide ions. This observation is consistent with the stabilization of the complexed cation by a mesomeric effect involving ligand p-π orbitals and filled metal d-π orbitals of the appropriate symmetry.

INTRODUCTION

Carbonium Ions

The direct observation of carbonium ions in solution by spectral techniques requires that the reaction generating the carbonium ion be only slightly endothermic and that there be no opportunity for their conversion to more stable entities (1). The fact that so much of the early attention was focused on the trityl cations has been attributed to their large resonance stabilization energies which favored the ionization process. Generally, these cations were generated in concentrated protic acids from the corresponding alcohols with an intense color accompanying cation formation. The color was attributed to electronic transitions within the conjugated π framework in analogy with the polymethine dyes.

Attempts to generate alkylcarbonium ions in a similar manner were not successful even for the t-butyl cation which, although formed, immediately underwent deprotonation, polymerization, fragmentation, cyclization, and complex rearrangement (2). It gradually became obvious that the environment of the carbonium ion had a profound effect on its stability, and the use of "superacids" by Olah and co-workers (3) provided a means of stabilizing inherently unstable cations in a sort of metastable state. In this

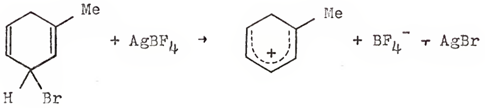
way alkylcarbonium ions were formed from the ionization of the corresponding alkyl fluorides in antimony pentafluoride. The energy required for the heterolytic cleavage of the C-F bond is compensated for by the strength of the Sb-F bond in forming SbF_6^- and also by solvation of the ions by the solvent.

The use of strong Lewis acids as solvents have provided a unique opportunity to directly observe carbonium ions whose existence could only be speculated. The stabilization of the anion formed along with the cation had become the key and quantitative estimates of the extra stabilization through coordination of the anion to the solvent in BF_3 solution.

$$X^- + BF_3 \rightarrow BF_3X^- \qquad (1)$$

have been obtained from thermochemical measurements, i.e., F^-, 75 kcal; OH^-, 79 kcal; Cl^-, 25 kcal; Br^-, 11 kcal (4,5).

Another means of stabilizing the anion is by the formation of an insoluble salt possessing a large lattice energy as for AgBr in the reaction (4,6)



(2)

These techniques for generating stable solutions of unstable cations appear to involve factors having little to do with the cation itself. Indeed, from a thermodynamic standpoint, the ionization of trityl alcohols in sulfuric acid is a consequence of the double protonation of the OH^- ion (4) with the stoichiometry having been elucidated from cryoscopic measurements as

$$Ph_3COH + 2H_2SO_4 \rightarrow Ph_3C^+ + H_3O^+ + 2HSO_4^- \qquad (3)$$

It is apparent that in order to investigate the internal factors which influence the stability in a series of carbonium ions, e.g., substituent effects, it is necessary that the anion formed in each case be the same. The equilibrium constants for ionization will then be governed mainly by the attributes of the carbonium ions.

The thermodynamic stability of a carbonium ion is a relative term whose definition is with reference to another species which is commonly the precursor from which the carbonium ion was derived. The stability is, then, a measure of the extent to which the carbonium ion is formed from the precursor. The transformations can be expressed in the form of equilibrium equations and one can calculate the free energy changes for these transformations if the equilibrium constants are known.

The equilibrium constants for the ionization of a series of trityl chlorides in nitroalkane solvents have been determined by Evans and co-workers (7) using visible spectroscopy. The trityl cations have an intense

absorption band in the visible region and the molar absorptivity for the absorption at λ_{max} has been obtained at a sufficiently high acid strength that the corresponding alcohol is completely converted to the carbonium ion. Evans has assumed that such ions would have the same molar absorptivities in selected nitroalkane solvents, and has employed this assumption in calculating their equilibrium concentrations. This assumption seems credible in view of the similarity of the spectra obtained in sulfuric acid and the nitroalkane solvents. Because of the low dielectric constants of the nitroalkane solvents employed the ionization was to ion pairs with no measurable dissociation of these; consequently, the equilibrium constants determined were for the process leading to ionization. To obtain a wider range of structural effects on equilibrium constants Evans added mercuric chloride to the system which stabilized the anion by complexation, forming $HgCl_3^-$. They found in this way that the effect of methyl substitution at the ortho and para positions was to stabilize the carbonium ion with respect to the unsubstituted trityl cation, whereas, chloro substitution at the same positions had a destabilizing effect. However, it was simply not feasible by direct experimental determination to explore the effect of other substituent groups which would involve variation of the equilibrium constants through many powers of ten.

The ionization of alcohols in acidic media has provided the most quantitative information concerning substituent

effects in the triaryl series of carbonium ions. This is due in large part to the work of Deno and co-workers (8) who adapted Hammett's definition of acidity functions (9) to the ionization of the triarylmethanols in acids such as H_2SO_4, HNO_3, and $HClO_4$. Thus, Deno defined an acidity function H_R for processes such as

$$ROH + H^+ = R^+ + H_2O \tag{4}$$

which had the form

$$H_R = -pK_{ROH} - \log C_{R^+}/C_{ROH} \tag{5}$$

where

$$pK_{ROH} = -\log a_{R^+}a_{H_2O}/a_{ROH}a_{H^+} \tag{6}$$

A table of H_R values was developed by following the change in absorbance at λ_{max} for several aryl carbonium ions as a function of the acid strength of the media. A value of pK_{ROH} can be determined by combining H_R with C_{R^+}/C_{ROH}, which is obtained from the spectrophotometric data. Values of ΔG corresponding to the formation of the carbonium ions can then easily be calculated from the values of pK_{ROH}, and provide quantitative evidence of the expected effect of electron-releasing and electron-withdrawing groups on the stability of the aryl cations.

Confirmation of the accuracy of the acidity function method over wide ranges of equilibrium constants in establishing a scale of relative stabilities came from the determination of reversible electrode reduction potentials.

These EMF measurements allowed the standard free energy change ΔG of reactions

$$R^{+} + 1/2(Ph_3CCPh_3) \;=\; Ph_3C^{+} + 1/2(R\text{-}R) \qquad (7)$$

to be measured for a series of para-substituted trityl cations R^{+} (10). Normalizing the free energies obtained for equation (4) by taking the $R^{+} = Ph_3C^{+}$ case as the zero of energy led to good agreement between the ΔG's for equations (7) and (4).

In conjunction with these spectral studies has been the use of cryoscopic and conductimetric measurements which have established conclusively that the formation of the triaryl cations in 98% sulfuric acid from the corresponding alcohols proceeds to completion and that the ions are completely dissociated. This conclusion would have been difficult to draw from spectral data because ion association has but a minor effect on spectra.

While the use of cryscopic, conductimetric, and visible spectroscopic techniques can indicate the concentration and aggregation of carbonium ions they provide little information as to the structure of the ions. This is where nmr spectroscopy has proved particularly illuminating, because the complex spin-spin coupling patterns often found are diagnostic of the proton's environment. The ^{19}F nmr spectra of fluorine-substituted trityl cations (11) and the ^{1}H nmr of the trityl cation (12) have indicated the equivalence of all three rings, supporting the proposed propellor-like structure for the ions.

Moodie, Connor, and Stewart (13) recorded the ^{1}H nmr spectra of several para-substituted trityl cations and found, as expected, that the ring protons and substituent protons were all shifted to lower fields, indicating less shielding of these protons in the carbonium ions than in the neutral compounds of similar structure, i.e., compared toluene with the para-tolyl cations and anisole with the para-methoxyphenyl cations. They observed a greater shift between toluene and the tri-para-tolylmethyl cation than between anisole and the tri-para-methoxyphenylmethyl cation. They interpreted this as showing the importance of hyperconjugative structures in the former case in spite of the greater contribution to stability that a methoxy substituent makes.

The interpretation of proton chemical shifts in terms of echoing the π-electron density at the carbon to which the proton is attached has been the subject of considerable theoretical projection. Schaefer and Schneider (14) provide evidence for a simple linear correlation between the proton chemical shift (δ) and the "excess" charge density (ρ) at the neighboring carbon atom, i.e.,

$$\Delta\delta = k\rho \tag{8}$$

where $\Delta\delta$ is the difference between the chemical shift in the ion and in a related neutral species. In the absence of perturbing effects from ring currents, magnetic anisotropy, ion association, and solvent, the correlation works. Without correcting for a contribution from ring currents to

the charge density, Schaefer and Schneider showed close agreement between their results for the trityl cation and those obtained in a SCF treatment. However, Fraenkel and Farnum (15) point out that the SCF model may be a poor choice for comparison in contrast to earlier conclusions.

In a series of benzylic cations Farnum (16) has noted a qualitative correlation between the position of the para-proton resonance and the extent of positive charge on the phenyl ring. Thus, when the ions were arranged in the anticipated order of increasing stabilization of the benzylic carbonium ion by electron release from the phenyl group, the para-proton resonance moved progressively downfield. No correlation was found to exist for the ortho or meta protons.

In the natural order of progress after finding that such a correlation exists one looks for a linear free energy relationship. Taft and McKeever (17) found that the chemical shift of the ^{19}F resonance was directly proportional to the stabilizing effect of the groups X and X' (Figure 1) on the corresponding carbonium ions without the fluorine substituent, i.e.,

$$\delta_F = c\Delta G \tag{9}$$

where ΔG was determined by EMF measurements (10). This result also provided justification for using ^{19}F chemical shifts as a measure of the π-electron density on the neighboring carbon atom.

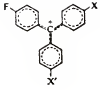


Fig. 1.--Fluorine-substituted trityl cation.

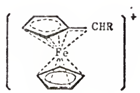


Fig. 2.--α-ferrocenylcarbonium ion stabilized by direct metal participation.

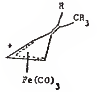


Fig. 3.--Cyclobutadienyltricarbonylironcarbinyl cation.

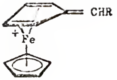
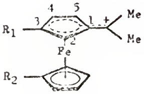


Fig. 4.--α-ferrocenylcarbonium ion stabilized by carbon-iron hyperconjugation.



a. $R_1 = R_2 = Me$

b. $R_1 = R_2 = (CH_2)_3$

Fig. 5.--Bridged α-ferrocenylcarbonium ion.

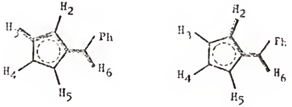


Fig. 6.--Zig-zag orientation for long range coupling.

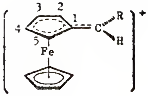


Fig. 7.--α-ferrocenylcarbonium ion.

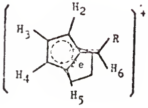


Fig. 8.--Hisatome and Yamakawa model for the structure of α-ferrocenylcarbonium ions.

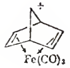


Fig. 9.--7-norbornadienyltricar-carbonyliron cation.

Fig. 10.--7-norbornadienyl cation.

Metal Atom Stabilized Carbonium Ions

Reports of the dramatic stabilization of carbonium ions by the formation of π-bonds to transition metal atoms brought an exciting new dimension to the chemical literature during the decade of the '60 s .

The metal carbonyl complexes of several cyclic and acyclic conjugated carbonium ions, e.g., tropylium (18), cyclopentadienyl (19), cyclohexadienyl (20), cycloheptadienyl (21), cyclooctatrienyl (22), allyl (23), and pentadienyl (24) cations, possess greater stabilities than their simple carbonium ion counterparts. The decrease in the electrophilicity of these complexed cations is indeed striking, e.g., π-cyclohexadienyltricarbonyliron fluoroborate can be recrystallized from water (20).

The two major factors which have contributed to the greater stabilities of these complexed cations have been viewed as the donor properties of the π-electrons and the "back donation" of electrons from the metal atom to the organic ligand through interaction of filled orbitals of the metal with vacant π-molecular orbitals of the cationic ligand (24).

In all of these ions the sp^2 hybridized carbon atoms are fixed in a completely <u>cissoid</u> configuration which conceivably allows each to be bonded directly to the metal atom. However, it has recently been shown that the solvolysis of several esters of <u>trans</u>-π-pentadienyliron tricarbonyls proceeded through cationic intermediates

having trans-configurations (25). This result was consistent with either direct nucleophilic participation by iron or with resonance involving the conjugated ligand, and iron not directly participating in the reactions.

In a geometrical sense these cationic intermediates of trans-configuration are analogous to the α-ferrocenylcarbonium ions, whose precise mode of stabilization is also a matter of considerable dispute.

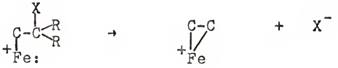
The stability of the α-ferrocenylcarbonium ions can be better appreciated when one realizes that these ions have no corresponding metal-free analogues unlike the complexed cations previously discussed. Their stability and structure are, of course, intimately involved, and since no X-ray determination of structure has been done, two different mechanisms for stabilization have been advanced and with them two opposing concepts of structure.

The concept of direct metal participation, i.e., involving the interaction of the nonbonding electrons located on the metal atom with the carbonium ion center, was first proposed as a possible mechanism by Richards and Hill (26), and later by Cais and co-workers (27). The general term "anchimeric assistance", first suggested by Winstein (28), has been used to describe this effect. A structural model supporting this mechanism (Figure 2) has the metal atom displaced in the cation towards the exocyclic carbon atom. The pmr spectral interpretation by Cais for a series of these ions provided support for such a molecular distortion. Thus, while protons H_2 and H_5 in ferrocene rings

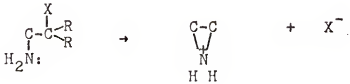
monosubstituted with electron-withdrawing groups are normally deshielded by about 20 Hz compared with protons H_3 and H_4, the relative chemical shift of these protons is reversed and their shielding difference (Δ) is greatly magnified in the carbonium ions. This is explained on the basis of a model (Figure 2) in which movement of the iron atom closer to the exo-cyclic carbon atom results in increased metal-ring bonding at $C_{2,5}$ and, more importantly, in increased shielding at $H_{2,5}$ and a decrease in shielding at $H_{3,4}$ due to the induced field caused by the anisotropy of the iron atom. Additionally, Δ showed a progressive decrease as electron-releasing groups were substituted at the carbonium center. This was interpreted as a reduction in the magnitude of the shift of the iron atom, since $H_{2,5}$ would experience less of a shielding effect from the magnetic anisotropy of the iron atom, resulting in a decrease in Δ .

The interpretation of the pmr spectral data for the cyclobutadienyltricarbonylironcarbinyl cation led Pettit and co-workers (29) to propose Figure 3 for its structure and it was suggested that the α-ferrocenyl cation might be formulated at the analogous exo-cyclic double bonded structure (Figure 4). Ware and Traylor (30) also adopted this model and suggested on the basis of kinetic data that no appreciable stabilization of the intermediate cation need be attributed to direct metal participation. Thus, in the case of the solvolyses of α-ferrocenylethyl derivatives the reported rate increases of about 10^{13} over the ethyl

derivatives were inordinately large for direct metal participation when compared to an increase of about 10^5 for participation of the β-amino group.



(10)



(11)

They contend that the large rate enhancement is comparable to the effect of an α-methoxy group on similar solvolyses

$$H_3CO\overset{X}{C} \rightarrow H_3C\overset{+}{O}{=}C + X^- \qquad (12)$$

The stability could then be related to the more conventional resonance effect involving the ring and the charged center (Figure 4) and designated as π-σ conjugation or carbon-iron hyperconjugation. It was, however, concluded by reference to analogous olefinic and carbonium ion systems that the pmr chemical shifts of the ring protons and the protons attached to the carbonium center could be explained by reference to either model.

A pmr study by Feinberg and Rosenblum (31) has suggested that the proposed distortion (Figure 2) does not occur. They found that for the cation (Figure 5a) and the bridged cation (Figure 5b), there was no significant difference in chemical shift of the di-substituted ring protons and the methyl protons at the carbonium center between the two.

This suggested a close similarity both in charge distribution within the cations and in their structures. Since a molecular distortion such as depicted in Figure 2 could only be imposed on the bridged cation at the cost of considerable valence angle distortion within the bridging group, no distortion for either ion was predicted on the basis of the pmr data.

Recently, long range coupling through the carbonium center was observed in a sophisticated pmr treatment by Hisatome and Yamakawa (32) in examining the spectra of α-ferrocenyl carbonium ions at 100 MHz by employing double resonance techniques. This type of long range coupling is possible when the two interacting nuclei are oriented in a coplanar zig-zag form (Figure 6). From this they concluded that the hybridization at the carbonium center is sp^2 and that the sp^2 plane and the ring are coplanar. In comparing their results for the cations (Figure 7) with the pmr data for 6-phenylfulvene the protons $H_{2,5}$ in the cation appeared at an unusually higher field than those in 6-phenylfulvene, while the protons $H_{3,4}$ appeared almost the same in both. In addition, the difference in chemical shifts between protons $H_{2,5}$ is about 0.4 ppm in the latter, but 0.75 ppm in the former. They rationalize these findings as support for a structure involving direct metal participation by iron. That is, on the formation of the cation the iron atom shifts towards the carbonium center. If the plane of the sp^2 orbital is co-planar with the ring, as previously mentioned, the iron atom would slide to the opposite direction from

the bulky substituent due to steric hindrance (Figure 8), which would result in proton H_5 resonating at the highest field due to the diamagnetic anisotropic effect of the iron atom or to an increase in the charge distribution at C_5 by donation of some electron density from the iron atom. They also consider this possible in the bridged carbonium ion (Figure 5b) if the iron atom shifts towards C_5, because of its tilted conformation caused by bridging with three methylene groups.

The differences between the interpretations presented have been subtle but distinct and the most recent work by Hisatome and Yamakawa is certainly compelling evidence for direct metal participation.

In any event, there is considerable delocalization of the positive charge, and comparison of the rates of solvolysis for the acetates of α-metallocenylmethanols with trityl acetate suggest that the ferrocenyl nucleus is almost as effective as three phenyl substituents, and there is a rate enhancement as the metal is changed to ruthenium and then osmium (33).

It should be mentioned, however, that Hill and Wiesner (34) have cast some doubt concerning the applicability of kinetic data in relationship to the structure of these ions. In a Hammett-Deno-type indicator acidity study, they showed that the thermodynamic stability of ferrocenyl carbonium ions was several powers of ten greater than kinetic studies indicated. Since the stability of carbonium ions are typically correlated with their rates of formation in solvol-

ysis reactions, they concluded that the carbonium ion was well beyond the transition state and, more importantly, likely to be different in geometry as well as energy.

In the event that the carbonium ion center can't interact directly with the metal atom and/or if the metal atom places other electronic limitations on the system the possibility of forming a less stable cation becomes a reality. It has been shown by Rausch and co-workers (35) that the 7-norbornadienyl cation (Figure 9) is destabilized by attachment of a metal atom. This cation is stabilized by homoallylic delocalization of the charge at C_7 (Figure 10). Bonding of the cation to iron prevents this homoallylic interaction with destabilization resulting.

Statement of the Problem

The stabilization of carbonium ions by the formation of π-bonds to metal atoms leads to the speculation of whether carbonium ions could be stabilized by the formation of σ-bonds to appropriate metal atoms or ions. One would like to generate these carbonium ions in high enough concentrations that identification by spectroscopic techniques would be applicable. The first criterion to be met, however, is the formation of a σ-bond between the metal species and the carbonium ion. This might most easily be accomplished by having a heterocyclic moiety attached to the carbonium ion center. Indeed, Richardson (36) has prepared a series of σ-bond metal complexes with 4-pyridyldiphenylmethanols, which are the precursors for the complexed 4-pyridyldi-

phenylmethyl cations. The selection of a thiazolyl moiety attached to the carbonium ion center seemed like a logical extension of this work.

The work of Kurkjy and Brown (37) provided the impetus for the preparation of the several new thiazolyldiphenylmethanols reported in this work, which has the thiazolyl moiety changing from 2-thiazolyl through 2,4-dimethyl-5-thiazolyl and the phenyls from the unsubstituted ring to *para*-tolyl and *para*-methoxyphenyl. This would allow the maximum exposure of structural effects to the elucidation of relative stabilities, and would greatly simplify the interpretation of the pmr spectral data.

Richardson has outlined possible mechanisms by which a transition metal ion can affect the stability of the carbonium ion to which it is complexed:

> Destabilization would result from inductive withdrawal accompanying formation of a dative σ bond, from resonance withdrawal of ligand π-electron density by empty metal *d* orbitals, or from electrostatic repulsion of the metal containing moiety if it itself is positive. Stabilization would arise with resonance donation of metal *d* electron density to empty π-symmetry ligand orbitals, with increased size of the charged species, with a negatively charged metal containing moiety, or with direct, through-space interaction of the positive center with the metal ion. The opposing factors, inductive withdrawal and increased size, are always operative and should not vary greatly from one metal ion to another of the same charge type. Donation or withdrawal of electron density to (from) the carbonium ion ligand would depend on the relative energies of the metal *d* and ligand molecular orbitals and on their occupancies (36).

The choice of palladium (II) as the metal species was guided by the relative inertness of its complexes, its low oxidation state, and the availability of filled _d_ orbitals which would conceivably interact with the π-framework of the carbonium ion to stabilize it by charge dispersal.

Relatively few complexes of thiazole or its derivatives have been isolated due more or less to a lack of interest rather than to any inherent instability of the complexes. The 2:1 complex of 4-methylthiazole (4-MeT) with palladium (II) is known (38) and has been prepared both by the reaction of bis(benzonitrile)palladium(II) chloride with 4-methylthiazole and the reaction of the tetrachloropalladate (II) ion with 4-methylthiazole. The far-infrared spectrum of $Pd(4\text{-}MeT)_2Cl_2$ suggested a _trans_ configuration for the square-planar complex isolated in both instances. The 2:1 complex of 4-methylthiazole with platinum(II) has been prepared from the tetrachloroplatinum(II) ion and was shown to have a _cis_ structure (39).

These results imply that the reactions of palladium(II) are thermodynamically controlled rather than kinetically controlled, and while the _cis_ complex may be initially formed it is converted quickly to the more stable _trans_ complex. In fact few ligands provide examples of _cis--trans_ isomerism in palladium(II) complexes, NH_3 being one of the notable exceptions. It is with this observation in mind that the 2:1 complexes of the thiazolyldiphenylmethanols with palladium(II) were prepared. Steric interactions would thus be minimized with these bulky ligands in positions _trans_ to

one another.

The present work focuses on the interpretation of the pmr and visible spectral data to establish criteria for the formation of the carbonium ions, as a means of relegating relative stabilities to the ions, and to determine the effect of complexation upon these stabilities.

The "ethanol" series of ligands was not studied in any detail for it was believed that the elimination of water to form the alkene would be the primary reaction in acidic media. Protonation of the olefin to form a tertiary carbonium ion is considered the logical sequential step and may warrant later attention.

As an aid to the reader who is inexperienced in this field of chemistry the structure of the p-methoxyphenyl member for each of the series studied is presented in Appendix 2.

EXPERIMENTAL

Synthesis

The preparation of all the alcohols (ligands) reported herein involved the reaction of either benzophenone, 4,4'-dimethylbenzophenone, or 4,4'-dimethoxybenzophenone with a thiazolyllithium reagent. The thiazolyllithium reagents were prepared by the exchange reaction between n-butyllithium and an appropriate thiazole derivative, e.g., 2-thiazolyllithium from 2-bromothiazole, 4-methyl-2-thiazolyllithium from 4-methylthiazole, 4,5-dimethyl-2-thiazolyllithium from 4,5-dimethylthiazole, 4-methyl-2-thiazolylmethyllithium from 2,4-dimethylthiazole, and 2,4-dimethyl-5-thiazolyllithium from 5-bromo-2,4-dimethylthiazole. With the exception of 2,4-dimethylthiazole, none of the thiazole derivatives was commercially available, i.e., the syntheses of the remaining thiazole compounds were required.

As with the reaction between any organolithium compound and a ketone, care was exercized to prevent moisture and oxygen from coming into contact with the reaction mixture. An atmosphere of dry nitrogen or argon was maintained in the reaction vessel and all solvents were previously dried by standard techniques. Tetrahydrofuran was employed as the solvent for reactions involving 4,4'-dimethoxybenzophenone,

which has limited solubility in diethyl ether.

The lithium ribbon, used in the preparation of n-butyllithium and obtained in 99.9% purity from Matheson Coleman & Bell, was cut into small strips and washed with petroleum ether prior to use to remove the protective coating of petrolatum. The required carbonyl compounds and n-buthylbromide were used as purchased from Matheson Coleman & Bell, Aldrich Chemical and Eastman Organic Chemicals Company.

Butyllithium was prepared according to the method of Gilman and co-workers (40). A solution of n-butylbromide in diethyl ether was added dropwise with stirring to a slurry of lithium in diethyl ether, while maintaining the temperature below 0^{o} with an ice--salt bath. After addition the mixture was stirred for two hours or until all the lithium had reacted. The temperature was lowered to -70^{o} by use of a dry ice--isopropanol bath and the thiazole derivative was added, followed by stirring for 30 minutes. The carbonyl compound, dissolved in either diethyl ether or tetrahydrofuran, was slowly added and stirring was continued for approximately three hours. Hydrolysis was accomplished by the addition of either dilute hydrochloric acid or distilled water and is described more fully together with the subsequent work-up in the individual description of the ligand preparations.

The palladium complexes were prepared by reaction of the tetrachloropalladate(II) ion with the appropriate ligand. Palladium(II) chloride was dissolved in either

methanol or acetone to which an equivalent amount of lithium chloride had been added. The lithium tetrachloropalladate(II) formed is soluble in these solvents. The ligand was introduced as a solid to the refluxing tetrachloropalladate(II) solution and stirring was continued until precipitation of the desired complex was essentially complete. The complexes were filtered, washed with diethyl ether, followed by distilled water and acetone and dried in vacuo over P_4O_{10}. This procedure was followed essentially as described for the preparation and isolation of each complex and as a result no individual experiments are discussed. The yields of complexes were consistently greater than 50%, with the elemental analyses given in Table 1. All the complexes melted with decomposition at temperatures in excess of 220°.

The preparation of the dibromopalladium(II) complex of 4-methyl-2-thiazolyldi(p-tolyl)methanol proceeded by dissolving $PdCl_2$ in acetone using a 200% excess of lithium bromide and stirring for 48 hours. The ligand was then added under reflux and following the precipitation of the complex the reaction mixture was worked up as in the case of the dichloro complexes.

2-thiazolyldiphenylmethanol

An ethereal solution of n-butyllithium, prepared from 18.0g (0.13 mole) of n-butylbromide and 2.1 g (0.3 mole) of lithium, was reacted at -70° with a solution of 16.4 g (0.10 mole) of 2-bromothiazole in ether. To the dark

reaction mixture was added 18.2 g (0.10 mole) of benzophenone, dissolved in ether. An ice--salt bath was now employed, and after stirring for one hour, 200 ml of 6 N HCl was slowly added to hydrolyze the reaction mixture. The aqueous layer gave an off-white precipitate upon neutralization which, after two successive recrystallizations from petroleum ether, had a sharp melting point of 114.5° lit. (38) mp 116-117° . The yield was 7.5 g (28%).

Anal. Calcd for $C_{16}H_{13}NOS$: C, 71.88; H, 4.90; N, 5.24.
Found: C, 71.76; H, 4.91; N, 5.34.

2-thiazolyldi(p-tolyl)methanol

The 2-thiazolyllithium, prepared from 0.2 mole n-butyllithium and 32.6 g (0.2 mole) of 2-bromothiazole, was reacted at -70° with an ethereal solution of 37.8 g (0.18 mole) of 4,4'-dimethylbenzophenone. After one hour at -70° an ice--salt bath was used and stirring was continued for two hours. With the temperature of the reaction mixture at -5°, hydrolysis occured upon the addition of dilute hydrochloric acid. The ether layer yielded an oil after the solvent had been stripped off. The oil, redissolved in ether and dried over Molecular Sieves 3A, yielded a tan solid upon concentration of the solution. Several recrystallizations from petroleum ether gave 10.0 g of product (19%) melting at 82-83°.

Anal. Calcd for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80; N, 4.74.
Found: C, 73.02; H, 5.90; N, 4.67.

2-thiazolylbis(p-methoxyphenyl)methanol

The preparation of 0.09 moles of 2-thiazolyllithium was followed by the addition of 0.05 moles of 4,4'-dimethoxybenzophenone, dissolved in several hundred milliliters of diethylether. After 30 minutes at -70° an ice--salt bath was employed and stirring was continued for two hours; the reaction mixture was hydrolyzed using distilled water. After filtering the reaction mixture and discarding a brown solid the ether layer yielded the desired product in an impure state. The ligand was purified by column chromatography over alumina using bezene as the eluant. The yield of 2 g (12%) had a melting point of 145-147°.

Anal. Calcd for $C_{18}H_{17}NO_3S$: C, 66.03; H, 5.23; N, 4.28. Found: C, 66.45; H, 5.26; N, 4.26.

4-methyl-2-thiazolyldiphenylmethanol

A light green solution results from the reaction at -70° between 9.9 g (0.1 mole) of 4-methylthiazole and 0.11 mole of n-butyllithium, prepared from 1.52 g (0.22 mole) of lithium and 15.07 g (0.11 mole) of n-butylbromide. The addition of an ethereal solution of 15.5 g (0.085 mole) of benzophenone with stirring for two hours is followed by hydrolysis using distilled water. After concentrating the ether layer it is dried over Molecular Sieves 3A. Petroleum ether was used to precipitate the product from the ether solution in a yield of 17.0 g (71%) having a melting point of 91°.

Anal. Calcd for $C_{17}H_{15}NOS$: C, 72.57; H, 5.37; N, 4.98. Found: C, 72.45; H, 5.43; N, 5.01.

4-methyl-2-thiazolyldi(p-tolyl)methanol

The preparation was similar to that of the phenyl analogue, except that 17.9 g (0.085 mole) of 4,4'-dimethylbenzophenone was used. After drying and concentrating the ether layer it yielded 14.1 g (56%) of product which when recrystallized from ether--petroleum ether melted at 91.5-92.5°.

Anal. Calcd for $C_{19}H_{19}NOS$: C, 73.75; H, 6.19; N, 4.53 Found: C, 73.83; H, 6.14; N, 4.50.

4-methyl-2-thiazolylbis(p-methoxyphenyl)methanol

The preparation was analogous to others in this series, except that a solution of 9.09 g (0.0375 mole) of 4-4'-dimethoxybenzophenone in tetrahydrofuran was reacted. The water layer was extracted several times with diethylether and the extracts combined; the solvent gave an oil when concentrated. Attempts were unsuccessful to get the oil to crystallize using the technique of drying over molecular sieves and treatment with petroleum ether. The oil after having been placed under vacuum over P_4O_{10} for about a week gradually began to crystallize. Several recrystallizations from ether--petroleum ether gave a pure product in 48% yield (6.1 g).

Anal. Calcd for $C_{19}H_{19}NO_3S$: C, 66.84; H, 5.61; N, 4.10. Found: C, 67.01; H, 5.75; N, 4.05.

4,5-dimethyl-2-thiazolyldiphenylmethanol

To an ethereal solution of n-butyllithium, prepared from 1.52 g (0.22 mole) of lithium and 15.07 g (0.11 mole) of n-butylbromide, was added 11.3 g (0.10 mole) of 4,5-dimethylthiazole at -70°, producing a light green mixture. This was followed by the addition of 15.5 g (0.085 mole) of benzophenone in ether; after stirring for three hours the mixture was hydrolyzed with distilled water. The ether layer, concentrated and dried over Molecular Sieves 5A, yielded 11.9 g (47%) of ligand upon the addition of petroleum ether. Recrystallization from diethylether--petroleum ether gave a melting point of 103-104° lit. (37) mp 105-105.5° .
Anal. Calcd for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80; N, 4.74.
Found: C, 73.17; H, 5.88; N, 4.72.

4,5-dimethyl-2-thiazolyldi(p-tolyl)methanol

The preparation of 4,5-dimethyl-2-thiazolyllithium proceeded as described above, and reaction with 17.9 g (0.085 mole) of 4,4'-dimethylbenzophenone followed; hydrolysis occurred upon the addition of distilled water. The ether layer produced an oil which crystallized on standing overnight; recrystallization from diethylether--petroleum ether yielded 6.7 g (24%) of product melting in the 77.0-79.5° range.
Anal. Calcd for $C_{20}H_{21}NOS$: C, 74.27; H, 6.54; N, 4.33.
Found: C, 73.73; H, 6.46; N, 4.28.

4,5-dimethyl-2-thiazolylbis(p-methoxyphenyl)methanol

This ligand was isolated as an oil in the reaction between 0.1 mole of 4,5-dimethyl-2-thiazolyllithium and 0.05 mole of 4,4,'-dimethoxybenzophenone. The oil was eluted through a column of alumina using a 5:1 mixture of hexane--chloroform. The effuent yielded a greenish-white solid which was recrystallized from petroleum ether to give the colorless product in 50% yield (9.9 g); melting point 143-144^{o} (dec).

Anal. Calcd for $C_{20}H_{21}NO_3S$: C, 67.58; H, 5.95; N, 3.94. Found: C, 67.60; H, 5.98; N, 3.88.

2,4-dimethyl-5-thiazolyldiphenylmethanol

The lithium intermediate, 2,4-dimethyl-5-thiazolyllithium, was prepared from 0.1 mole of n-butyllithium and 19.2 g (0.1 mole) of 5-bromo-2,4-dimethylthiazole at -70^{o}. An ethereal solution of 18.2 g (0.1 mole) of benzophenone was slowly added, and the mixture was hydrolyzed using distilled water after stirring for four hours. The resulting white precipate was recrystallized from chloroform to yield 2.1 g (7%) of product; melting point 170.5-171.5^{o}.

Anal. Calcd for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80; N, 4.74. Found: C, 73.20; H, 5.67; N, 4.73.

2,4-dimethyl-5-thiazolyldi(p-tolyl)methanol

Following the preparation of 2,4-dimethyl-5-thiazolyllithium from 0.11 mole of n-butyllithium and 0.1 mole of

5-bromo-2,4-dimethylthiazole, an ethereal solution of 21.0 g (0.1 mole) of 4,4'-dimethylbenzophenone was added and stirring continued for three hours at -70°. Upon hydrolyzing with distilled water, 12.9 g of product precipitated. The ether layer, extracted with dilute hydrochloric acid and neutralized, gave an additional 2.3 g. The combined yield of 47% was recrystallized from diethylether--petroleum ether; melting point 152.5-154-5°.

Anal. Calcd for $C_{20}H_{21}NOS$: C, 74.27; H, 6.54; N, 4.33. Found: C, 74.35; H, 6.62; N, 4.29.

2,4-dimethyl-5-thiazolylbis(p-methoxyphenyl)methanol

The reaction between 0.1 mole of 2,4-dimethyl-5-thiazolyllithium and 0.05 mole of 4,4'-dimethoxybenzophenone was worked up as usual; the product precipitated as a brownish-white solid upon hydrolysis. This was purified using column chromatography over alumina with a 5:1 mixture of hexane-chloroform as eluant. The ligand was isolated in 69% yield (12.3 g); melting point 141-142° (dec).

Anal. Calcd for $C_{20}H_{21}NO_3S$: C, 67.58; H, 5.95; N, 3.94 Found: C, 67.38; H, 6.00; N, 3.88.

2-(4-methyl-2-thiazolyl)-1,1-diphenylethanol

The preparation of the yellowish-green solution of 4-methyl-2-thiazolylmethyllithium from 0.20 moles of n-butyllithium and 22.6 g (0.20 mole) of 2,4-dimethylthiazole was followed by reaction with an ethereal solution of 27.3 g (0.15 mole) of benzophenone for two hours at -70°.

The reaction mixture, allowed to warm up to 0°, was hydrolyzed using 6 M HCl. The white precipitate, recrystallized from methanol, turned yellow upon melting in excess of 180°, characteristic of a thiazolium hydrochloride salt. The hydrochloride was neutralized with an aqueous solution of 3 M sodium hydroxide and extracted with diethylether. The ether extract yielded a solid, which when recrystallized from methanol, gave 27.0 g (61%) of the desired compound; melting point 150.0-151.5°.

Anal. Calcd for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80; N, 4.74. Found: C, 72.97; H, 5.77; N, 4.65.

2-(4-methyl-2-thiazolyl)-1,1-di(p-tolyl)ethanol

The reaction proceeds by the initial preparation of 4-methyl-2-thiazolylmethyllithium from 0.20 mole of n-butyllithium and 0.20 mole of 2,4-dimethylthiazole. After the addition of 0.15 mole of 4,4'-dimethylbenzophenone and stirring for one hour at -70°, the cooling bath was removed; the mixture was hydrolyzed with dilute hydrochloric acid when the temperature had risen to 0°. The white precipitate was recrystallized from methanol to give 12.0 g (25%) of product; melting point 118-119°.

Anal. Calcd for $C_{20}H_{21}NOS$: C, 74.27; H, 6.54; N, 4.33. Found: C, 74.39; H, 6.45; N, 4.26.

2-(4-methyl-2-thiazolyl)-1,1-bis(p-methoxyphenyl)ethanol

The reaction between 0.11 mole of n-butyllithium and 0.10 moles of 2,4-dimethylthiazole was followed by the

addition at -70° of 0.025 mole of 4,4'-dimethoxybenzophenone in tetrahydrofuran. After two hours the cooling bath was removed and stirring was continued for an additional one hour; the mixture was hydrolyzed using distilled water. The ether layer gave a solid which on recrystallization from methanol yielded 4.8 g (54%) of ligand; melting point $113-114^{\circ}$.

Anal. Calcd for $C_{20}H_{21}NO_3S$: C, 67.58; H, 5.95; N, 3.94. Found: C, 67.55; H, 5.95; N, 3.86.

2,3,4-trimethyl-5-(hydroxydi(p-tolyl)methyl)thiazolium iodide

The methyl iodide salt was prepared by dissolving 0.76 g of 2,4-dimethyl-5-thiazolyldi(p-tolyl)methanol in 25 ml of methyl iodide and allowing the colorless solution to stand overnight. Reaction resulted in an orange solution and the presence of a solid; diethyl ether was slowly added to precipitate more of the salt. The methyl iodide salt was dissolved in boiling water and the solution filtered to remove a purple residue. Following treatment with bone charcoal the filtrate yielded a white solid which was washed with distilled water and dried over P_4O_{10} *in vacuo*. The yield was approximately 30%; melting point 240° (dec).

Anal. Calcd for $C_{21}H_{24}INOS$: C, 54.20; H, 5.20; N, 3.00. Found: C, 54.39; H, 5.32; N, 3.01.

2-bromothiazole

This compound was prepared from commercially available 2-aminothiazole by employing a modification of the procedure

of Ganapathi and Venkataraman (41). Practical grade 2-aminothiazole was dissolved in acetone and 85 percent phosphoric acid was slowly added to the dark solution, resulting in the precipitation of a tan solid, and identified by elemental analysis as the 1:1 adduct of 2-aminothiazole and phosphoric acid. The temperature of a solution of 119 g (0.6 mole) of the adduct in 185 ml of 85 percent phosphoric acid was lowered to -5^{o} and 118 ml of 71 percent nitric acid was slowly added. The mixture was diazotized with an aqueous solution of 48 g of sodium nitrite being allowed to flow beneath the surface of the solution through the stem of a separatory funnel. After stirring for 30 minutes the diazonium solution was added to an aqueous solution of 200 g of copper sulfate and 176 g of sodium bromide. The evolution of nitrogen was immediate and ceased in about 20 minutes. Following neutralization with sodium hydroxide, the mixture was steam distilled with 2-bromothiazole passing over in the distillate as a yellow oil. The distillate was extracted with ether, concentrated, dried (Na_2SO_4), and fractionally distilled to give 40 g (43%) of product.

4,5-dimethylthiazole

This compound was prepared by following the procedure of Kurkjy and Brown (42). A slurry of 67.5 g (0.32 mole) of phosphorus pentasulfide in 100 ml of dry dioxane was reacted with 66 g (1.47 mole) of formamide, with cooling in an ice bath when the flask became warm. The slow dropwise addition of 151 g (1.0 mole) of 3-bromo-2-butanone maintained a

gentle reflux, and avoided the tar formation which accompanied rapid refluxing of the reaction mixture. The reaction mixture was refluxed for one hour after the reaction had subsided, and 125 ml of 3 M HCl were added, followed by refluxing for one additional hour. The mixture was steam distilled to remove most of the dioxane, made basic with sodium hydroxide, and steam distilled again. The distillate was saturated with potassium carbonate and extracted with ether. The ether extract, concentrated and dried (Na_2SO_4), was fractionally distilled at reduced pressure to yield 60 g (57%) of 4,5-dimethylthiazole. Prior to use it was distilled over calcium hydride.

4-methylthiazole

The preparation was similar to that for 4,5-dimethylthiazole using 92.5 g (1.0 mole) of freshly distilled 3-chloro-2-propanone. The yield was 50 g (50%), and prior to use it was distilled over calcium hydride.

5-bromo-2,4-dimethylthiazole

This thiazole derivative was prepared from 2,4-dimethylthiazole by employing a modification of the method of Mikhailov and Bronovitskaya (43). To a slurry of 37.6 g (0.23 mole) of N-bromosuccinimide in 100 ml of dry carbon tetrachloride was added 22.6 g (0.20 mole) of 2,4-dimethylthiazole. The reaction mixture was gently refluxed for one hour, followed by shaking with a dilute aqueous solution of sodium hydroxide. The organic layer was dried (Na_2SO_4) and

fractionally distilled under reduced pressure. The colorless product was identified by its pmr, which indicated that bromination was essentially complete. Since the product decomposes upon exposure to light and air, it was stored under nitrogen in an amber bottle, and prior to use it was distilled. The yield was 21.3 g (55%).

Elemental Analyses

The carbon, hydrogen, and nitrogen elemental analyses were performed by either Galbraith Laboratories, Inc., or Atlantic Microlab, Inc. No special handling techniques were required for the ligands. Some of the palladium complexes tended to be hygroscopic; drying at 120° and handling in the dry box alleviated any problems. Palladium content of the complexes was determined by a standard gravimetric technique, i.e., digestion in concentrated acid followed by precipitation of the dimethylglyoxime complex of palladium.

Spectra

Visible Spectra

The visible absorption spectra were obtained from a Cary Model 14 recording spectrophotometer.

Proton Magnetic Resonance Spectra

The pmr spectra were obtained at 60 MHz using a Varian Model A-60A spectrometer. All solutions were filtered prior to running the spectra to remove dust and magnetic particles. Solvents employed were deuterochloroform (Silanor-C, minimum isotopic purity 99.8 atom percent

deuterium, Merck and Co.), and perchloric acid (70-72 percent by weight, Allied Chemical).

Electron Paramagnetic Resonance Spectra

The epr spectra were obtained from a Varian Model E-3 spectrometer.

RESULTS

Elemental Analyses

Elemental analyses for the ligands are included in the individual description of their preparations and were found to consistently agree with theory. Elemental analyses for the corresponding palladium complexes are presented in Table 1.

Visible Spectra

General Remarks

Stock solutions of each ligand in glacial acetic acid were prepared and diluted with 70-72 percent perchloric acid to generate each of the cations at a concentration of approximately 2×10^{-5}M, sufficient to obtain a visible spectrum. Accordingly, 1 ml of stock solution was diluted to 25 ml in a volumetric flask with 70-72 percent perchloric acid; the resulting mixture corresponded to 69 weight-percent perchloric acid as determined from specific gravity measurements.

Stock solutions of the palladium complexes in glacial acetic acid could not be prepared because of the virtual insolubility of the complexes in non-reacting or non-polar solvents. The complexes were dissolved directly in 69 percent perchloric acid and the spectra were run immediately.

TABLE 1

ELEMENTAL ANALYSES

Complex, $PdCl_2(LOH)_2$	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Nitrogen, % Calcd	Nitrogen, % Found	Palladium, % Calcd	Palladium, % Found
2-thiazolyl series								
LOH = $(2\text{-}C_3H_2NS)C(OH)X_2$								
X =								
$-C_6H_5$	53.99	53.90	3.68	3.69	3.93	3.99	14.94	14.98
-p-$CH_3C_6H_4$	56.29	56.46	4.46	4.51	3.65	3.65	13.86	13.75
-p-$OCH_3C_6H_4$	51.96	51.98	4.12	4.30	3.37	3.32	12.79	12.98
4-methyl-2-thiazolyl series								
LOH = $(4\text{-}CH_3\text{-}2\text{-}C_3HNS)C(OH)X_2$								
X =								
$-C_6H_5$	55.18	54.91	4.08	4.24	3.78	3.71	14.38	-
-p-$CH_3C_6H_4$	57.40	57.66	4.82	4.79	3.52	3.55	13.38	12.97
-p-$CH_3C_6H_4$[a]	51.57	51.77	4.33	4.37	3.16	3.08	12.02	11.93
-p-$OCH_3C_6H_4$	53.06	52.92	4.45	4.40	3.26	3.26	12.37	12.43

TABLE 1--Continued

Complex, $PdCl_2(LOH)_2$	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Nitrogen, % Calcd	Nitrogen, % Found	Palladium, % Calcd	Palladium, % Found
4,5-dimethyl-2-thiazolyl series								
LOH = $(4,5\text{-}(CH_3)_2\text{-}2\text{-}C_3NS)C(OH)X_2$								
X =								
$-C_6H_5$	56.29	54.01	4.46	4.42	3.65	3.59	13.86	-
-p-$CH_3C_6H_4$[b]	55.80	55.94	5.39	5.32	3.25	3.12	12.37	-
-p-$OCH_3C_6H_4$	54.11	53.92	4.73	4.73	3.15	3.07	11.98	11.99
2,4-dimethyl-5-thiazolyl series								
LOH = $(2,4\text{-}(CH_3)_2\text{-}5\text{-}C_3NS)C(OH)X_2$								
X =								
$-C_6H_5$	56.29	56.28	4.46	4.47	3.65	3.57	13.86	14.06
-p-$CH_3C_6H_4$	58.29	58.24	5.14	5.29	3.40	3.33	12.91	-
-p-$OCH_3C_6H_4$	54.11	54.36	4.73	4.66	3.15	3.20	11.98	11.60

[a] $PdBr_2(LOH)_2$

[b] $PdCl_2(LOH)_2 \cdot 2H_2O$

The complexes were often completely dissociated within several hours to yield the free carbonium ions.

Figures 11-19 illustrate the absorption spectra obtained for several of the free cations together with their corresponding palladium complexes.

The absorptivity of the 2-thiazolyldiphenylmethyl cation rapidly decreased with time. This decrease is reflected in the smaller molar absorptivity of this cation as compared with the others (Table 2); no attempt was made to extrapolate the absorbance to zero time in calculating the molar absorptivity.

Table 2 lists the visible absorption data for each set of cations -- free and complexed -- observed in 69 percent perchloric acid. The assumption is made that at this acid concentration the arylmethanols are completely converted to the corresponding carbonium ions having the indicated molar absorptivities.

Dilution Effects

The linear relationship between the absorbance of a solute and its concentration, as expressed by Beer's Law, is not expected to hold in cases where the solute and solvent are involved in complex equilibria. In acid/base systems, for example, changes in the pH can result in non-linearity. In fact, it is because this situation arises in the study of the visible absorption spectra of carbonium ions in acidic media at different acid concentrations that a comparison of the difference between the observed relationship and that

TABLE 2

VALUES OF λ_{max} AND ϵ FOR SEVERAL TRIARYLMETHYL CATIONS -- FREE AND COMPLEXED -- IN PERCHLORIC ACID

Triarylmethanol	Free[a]		Complexed[b]	
	λ_{max}	$\epsilon(x10^{-4})$	λ_{max}	$\epsilon(x10^{-4})$
2-thiazolyl series				
ROH = $(2\text{-}C_3H_2NS)C(OH)X_2$				
X =				
$-C_6H_5$	502	0.82	453	0.73
	438	0.62		
$-\underline{p}\text{-}CH_3C_6H_4$	541	3.89	527	5.77
	4.18	1.78	458	4.62
$-\underline{p}\text{-}OCH_3C_6H_4$	591	4.68	567	10.00
	415	1.48	435	3.38
4-methyl-2-thiazolyl series				
ROH = $(4\text{-}CH_3\text{-}2\text{-}C_3HNS)C(OH)X_2$				
X =				
$-C_6H_5$	463	1.62	487	3.12
$-\underline{p}\text{-}CH_3C_6H_4$	537	3.88	512	7.22
	448	2.29	512[c]	8.00
$-\underline{p}\text{-}OCH_3C_6H_4$	588	4.50	555	11.12
	438	1.64	453	3.54

[a] HR^{+2}

[b] $PdCl_2R_2^{+2}$

[c] $PdBr_2R_2^{+2}$

[d] N-methyl iodide

Table 2--Continued

Triarylmethanol	Free[a]		Complexed[b]	
	λ_{max}	$\epsilon(x10^{-4})$	λ_{max}	$\epsilon(x10^{-4})$
4,5-dimethyl-2-thiazolyl series				
ROH = $(4,5\text{-}(CH_3)_2\text{-}2\text{-}C_3NS)C(OH)X_2$				
X =				
$-C_6H_5$	488	3.92	483	4.78
$-\underline{p}\text{-}CH_3C_6H_4$	529 492	4.00 3.76	507	11.00
$-\underline{p}\text{-}OCH_3C_6H_4$	585 465	4.78 2.45	552 482	11.00 5.28
2,4-dimethyl-5-thiazolyl series				
ROH = $(2,4\text{-}(CH_3)_2\text{-}5\text{-}C_3NS)C(OH)X_2$				
X =				
$-C_6H_5$	453	3.21	461	9.34
$-\underline{p}\text{-}CH_3C_6H_4$	497 419	4.73 2.02	476	11.59
$-\underline{p}\text{-}CH_3C_6H_4$[d]	497 422	5.58 2.37		
$-\underline{p}\text{-}OCH_3C_6H_4$	543 415	7.09 2.20	526 445	13.91 7.43

Fig. 11.--Visible spectra of the 2-thiazolyldi(p-tolyl)-methyl cation -- free and complexed -- in perchloric acid.

Symbol	Cation	λ_{max}	ϵ_{max}
- - - - -	free	541	3.89×10^4
		418	1.78×10^4
— · — · —	complexed	527	5.77×10^4
		458	4.62×10^4

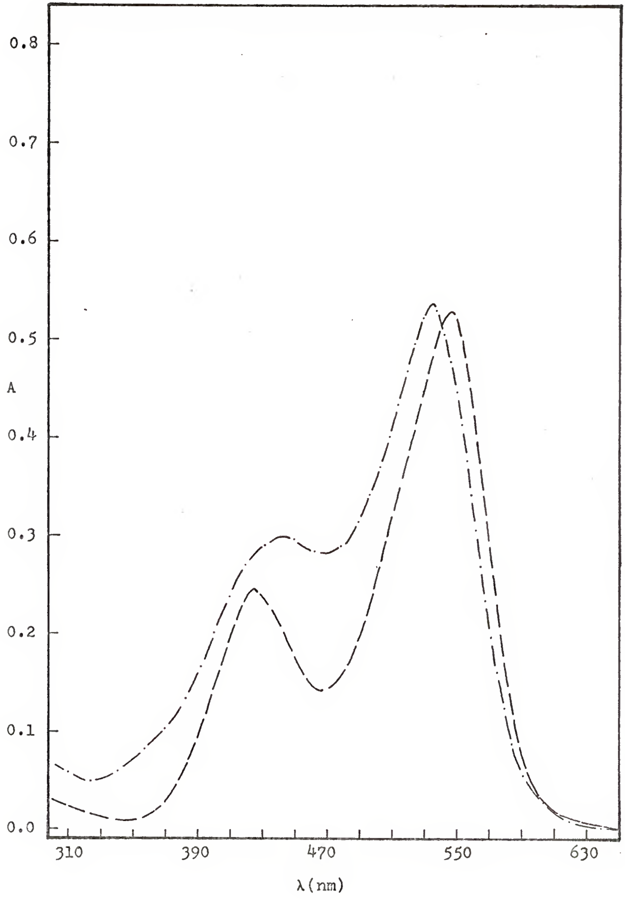

0.8
0.7
0.6
0.5
A
0.4
0.3
0.2
0.1
0.0
310
390
470
550
630
λ(nm)

Fig. 12.--Visible spectra of the 2-thiazolylbis(p-methoxyphenyl)methyl cation -- free and complexed -- in perchloric acid.

Symbol	Cation	λ_{max}	ϵ_{max}
– – – – –	free	591	4.68×10^4
		415	1.48×10^4
– · – · –	complexed	567	1.00×10^5
		435	3.38×10^4

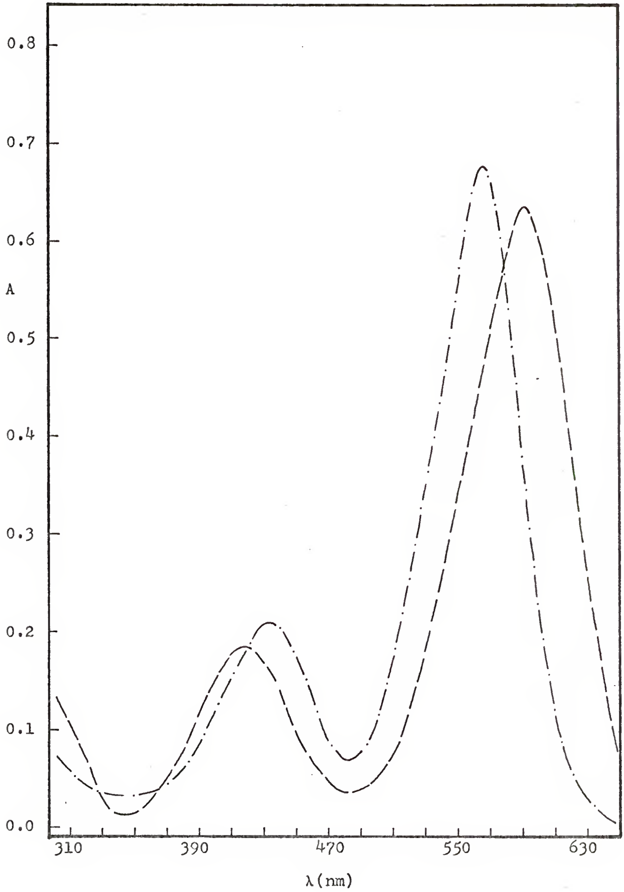

0.8
0.7
0.6
A
0.5
0.4
0.3
0.2
0.1
0.0
310
390
470
550
630
λ(nm)

Fig. 13.--Visible spectra of the 4-methyl-2-thiazolyldi-(*p*-tolyl)methyl cation -- free and complexed -- in perchloric acid.

Symbol	Cation	λ_{max}	ϵ_{max}
- - - - -	free	537	3.88×10^4
		448	2.29×10^4
- · - · -	complexed[a]	512	7.22×10^4
· · · · ·	complexed[b]	512	8.00×10^4

[a] $PdCl_2L_2^{+2}$

[b] $PdBr_2L_2^{+2}$

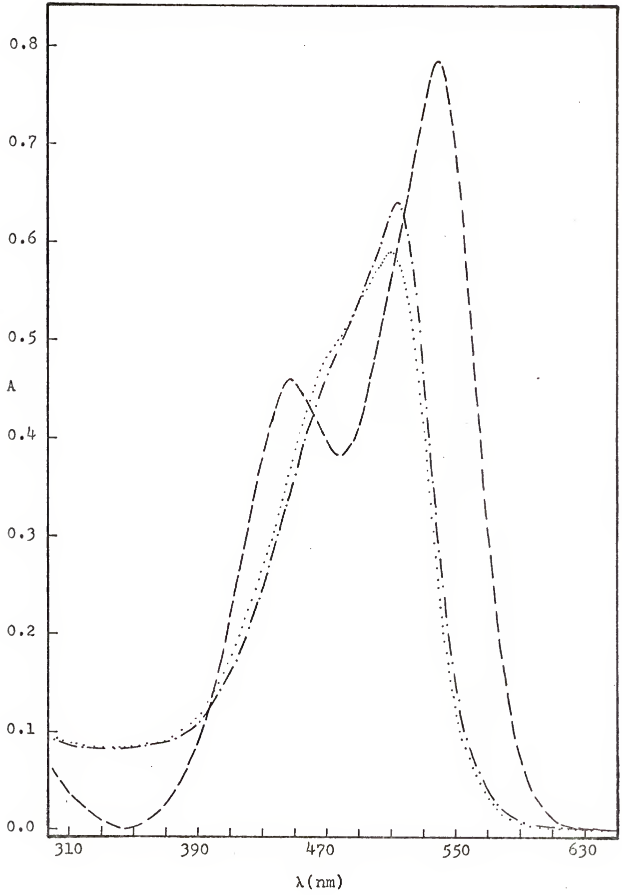

0.8
0.7
0.6
0.5
A
0.4
0.3
0.2
0.1
0.0
310
390
470
550
630
λ(nm)

Fig. 14.--Visible spectra of the 4-methyl-2-thiazolylbis(p-methoxyphenyl)methyl cation -- free and complexed -- in perchloric acid.

Symbol	Cation	λ_{max}	ϵ_{max}
- - - - -	free	588	4.50×10^4
		438	1.64×10^4
- · - · -	complexed	555	1.12×10^5
		453	3.54×10^4

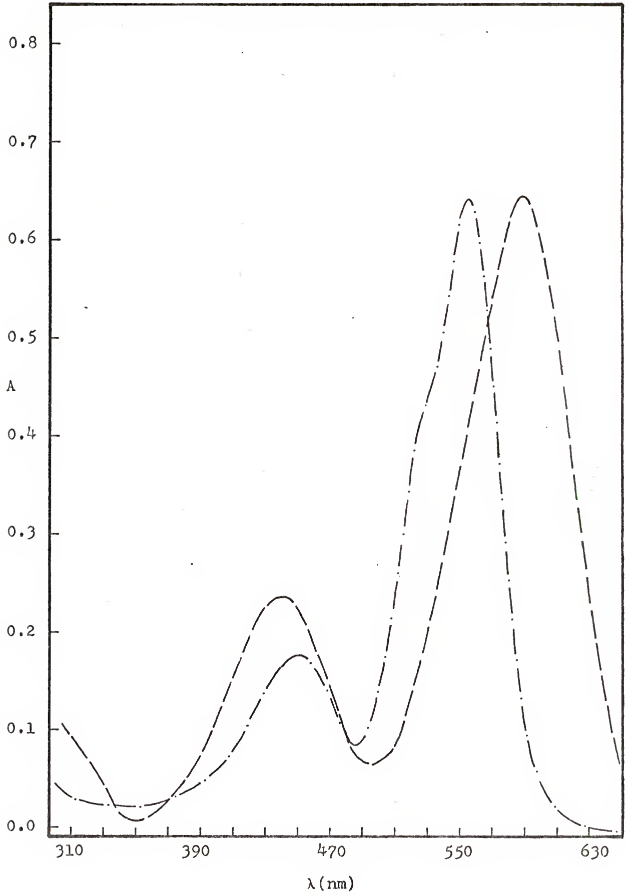

0.8
0.7
0.6
0.5
A
0.4
0.3
0.2
0.1
0.0
310
390
470
550
630
λ(nm)

Fig. 15 .--Visible spectra of the 4,5-dimethyl-2-thiazolyldi(p-tolyl)methyl cation -- free and complexed -- in perchloric acid.

Symbol	Cation	λ_{max}	ϵ_{max}
- - - - -	free	529	4.00×10^4
		492(sh)	3.76×10^4
- · - · -	complexed	507	1.10×10^5

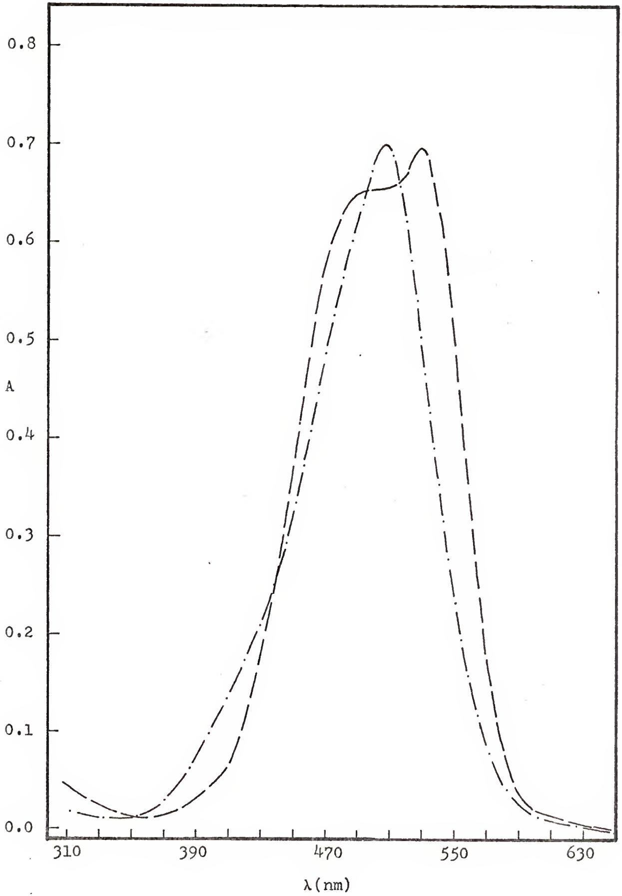

0.8
0.7
0.6
0.5
A
0.4
0.3
0.2
0.1
0.0
310
390
470
550
630
λ(nm)

Fig.16 .--Visible spectra of the 4,5-dimethyl-2-thiazolylbis(p-methoxyphenyl)methyl cation -- free and complexed -- in perchloric acid.

Symbol	Cation	λ_{max}	ϵ_{max}
– – – – –	free	585	4.78×10^4
		465	2.45×10^4
– • – • –	complexed	552	1.10×10^5
		482	5.28×10^4

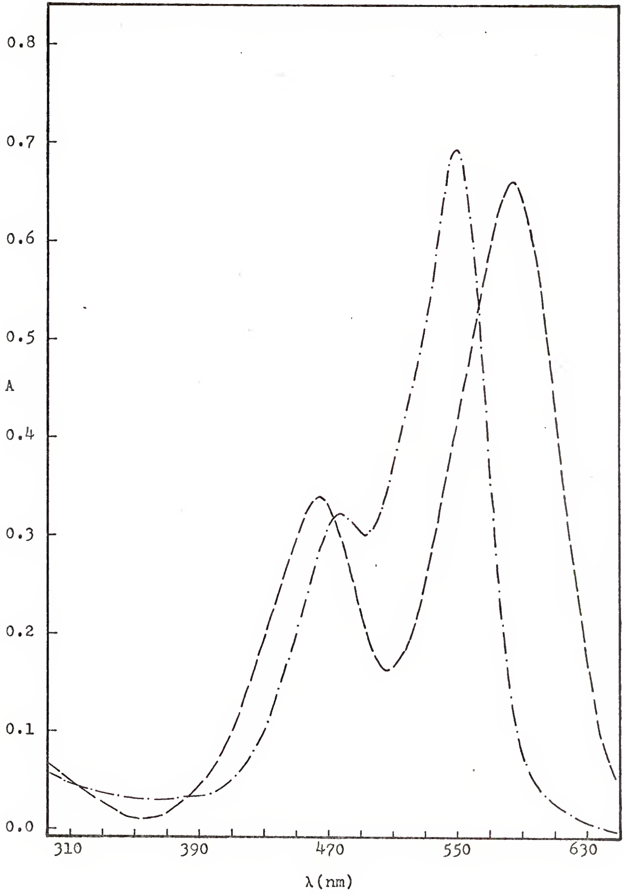

0.8
0.7
0.6
0.5
A
0.4
0.3
0.2
0.1
0.0
310
390
470
550
630
λ(nm)

Fig.17 .--Visible spectra of the 2,4-dimethyl-5-thiazolyldiphenylmethyl cation -- free and complexed -- in perchloric acid.

Symbol	Cation	λ_{max}	ϵ_{max}
- - - - -	free	453	3.21×10^4
- • - • -	complexed	461	9.34×10^4

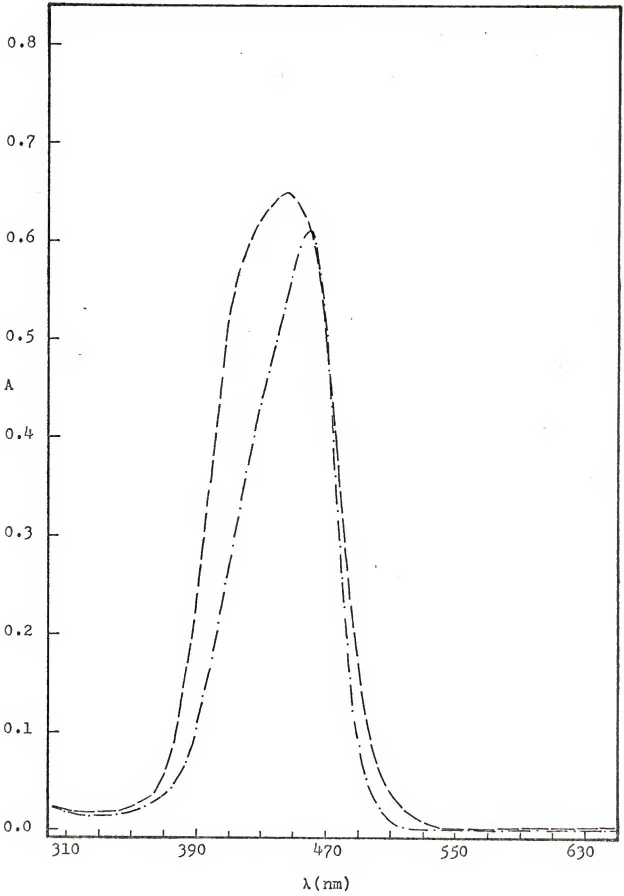
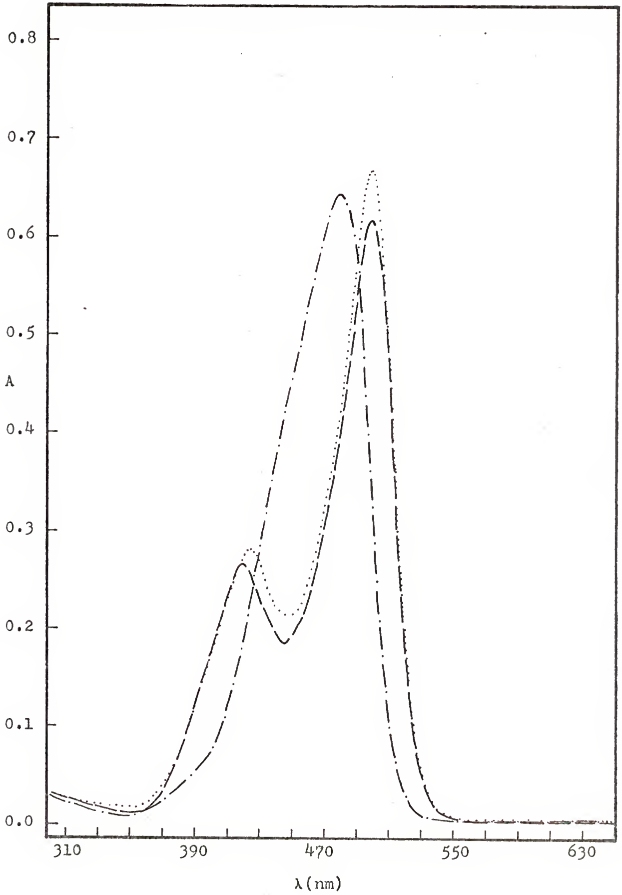

0.8
0.7
0.6
0.5
A
0.4
0.3
0.2
0.1
0.0
310
390
470
550
630
λ(nm)

Fig.18 .--Visible spectra of the 2,4-dimethyl-5-thiazolyldi(p-tolyl)methyl cation -- free and complexed -- in perchloric acid.

Symbol	Cation	λ_{max}	ϵ_{max}
– – – – –	free	497	4.73×10^4
		419	2.02×10^4
– · – · –	free[a]	497	5.58×10^4
		422	2.37×10^4
· · · · ·	complexed	476	1.16×10^5

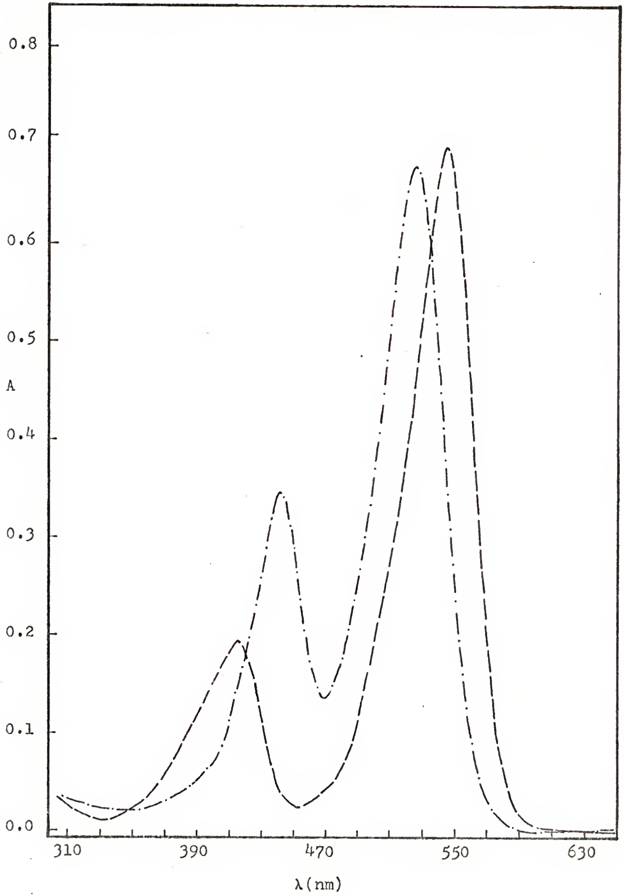
[a] N-methyl iodide



0.8
0.7
0.6
0.5
A
0.4
0.3
0.2
0.1
0.0
310
390
470
550
630
λ(nm)

Fig.19 .--Visible spectra of the 2,4-dimethyl-5-thiazolylbis(p-methoxyphenyl)methyl cation -- free and complexed -- in perchloric acid.

Symbol	Cation	λ_{max}	ϵ_{max}
- - - - -	free	543	7.09×10^4
		415	2.20×10^4
- . - . -	complexed	526	1.39×10^5
		445	7.43×10^4


0.8
0.7
0.6
0.5
A
0.4
0.3
0.2
0.1
0.0
310
390
470
550
630
λ(nm)

predicted by Beer's Law may enable a quantitative as well as a qualitative ordering of their relative stabilities.

The changes in the intensity of the visible absorption of the cations, caused by the addition of measured amounts of water to their perchloric acid solutions, were followed. The water was added dropwise to a known volume (2 ml) of perchloric acid solution contained in a cuvette and the absorbance at λ_{max} was measured to ± 0.001 absorbance units. The addition of water to these solutions was found to progressively shift λ_{max} by as much as four to five nanometers total toward shorter wavelengths for the free cations. For the complexed cations the shifts were of equivalent magnitude but toward longer wavelengths. The absorbance was measured after each dilution at the new λ_{max} rather than at the initial λ_{max}.

In the concentrations ranges employed the volume of the mixture could not be expressed as an exact sum of the volumes of perchloric acid and water. The actual volume of the solution obtained by the addition of each drop of water was calculated by using percent by weight--density data reported in the literature (44). A derivation of the conversion relationships employed is given in Appendix 1. The physical limitations of the cuvette used allowed a maximum addition of 30 drops of water to the initial sample volume.

The sum of the concentrations of carbonium ion and alcohol after each dilution was calculated by multiplying the initial molar concentration by the ratio of the initial

volume to the actual volume after each dilution. However, in plotting the data it was more convenient to treat this sum of the initial molar concentrations as a constant that was divided into the sum of the concentrations of carbonium ion and alcohol measured after each dilution. This term is referred to as the <u>dilution fraction</u>. What this does in effect is to eliminate the necessity of having to know the initial concentration; thus, the alcohol precursor did not need to be weighed. A Beer's Law plot, showing the decrease in absorptivity due to simple dilution, was drawn using the initial absorbance value as one point and the projected absorbance corresponding to a dilution of 30 percent as the other.

The absorbance values recorded for related pairs of carbonium ions, i.e., both free and complexed, were in most cases normalized so that the Beer's Law plot for each would have the same slope, making qualitative comparisons easier. The normalization technique was applied in the following manner. After obtaining the dilution data for a related pair of carbonium ions -- free and complexed -- the initial absorbance of the complexed cation was set equal to that for the free cation by the required multiplication factor, e.g., if $A_{initial}$ is 0.900 for that of the free cation whereas that of the complexed cation is 1.000, then the multiplication factor is 0.900. The succeeding absorbance values for the complexed cation were multiplied by this factor and plotted as described. Since the absissa of the plot remains unaltered this normalization technique is permissible from an algebraic standpoint.

The dilution curves for the 2,4-dimethyl-5-thiazolyl-bis(p-methoxyphenyl)methyl cation and its palladium complex followed Beer's Law throughout the addition of 30 drops of water necessitating the use of 46 percent perchloric acid as the solvent for generating the cation prior to running the titration.

Dilution Curves

Using a series of triarylmethanols as indicators, Deno developed an acidity function H_R, which measures the capacity of a medium to ionize the indicators. In Table 3 are listed the H_R values corresponding to several different weight percent perchloric acid solutions. A smooth curve was drawn through the points of a plot of H_R versus weight percent perchloric acid and was extrapolated to 65 percent perchloric acid; this curve is presented in Figure 20. Values of H_R for fractional weight percentages of perchloric acid were read directly off a blow-up of this curve on graph paper and are listed in Table 4 for dilutions at which subsequent calculations of the equilibrium constants were made.

Having the weight percent/H_R information together with the value of log $C_{HR^{+2}}/C_{HROH^{+1}}$ one can calculate from Equation 13 the $pK_{HROH^{+1}}$ for the equilibrium between the protonated alcohol and carbonium ion (Equation 14). The value of $C_{HR^{+2}}/C_{HROH^{+1}}$ after each dilution is obtained from the titration data as a ratio of absorbances. The concentration of HR^{+2} is set equal to the absorbance measured at

TABLE 3

VALUES OF H_R IN AQUEOUS PERCHLORIC ACID[a] AT 25°

%$HClO_4$	$-H_R$
30.0	3.79
35.0	4.61
40.0	5.54
42.0	5.95
44.0	6.38
46.0	6.82
48.0	7.31
50.0	7.86
52.0	8.45
54.0	9.05
56.0	9.68
58.0	10.37
60.0	11.14

[a]Deno et al. (45)

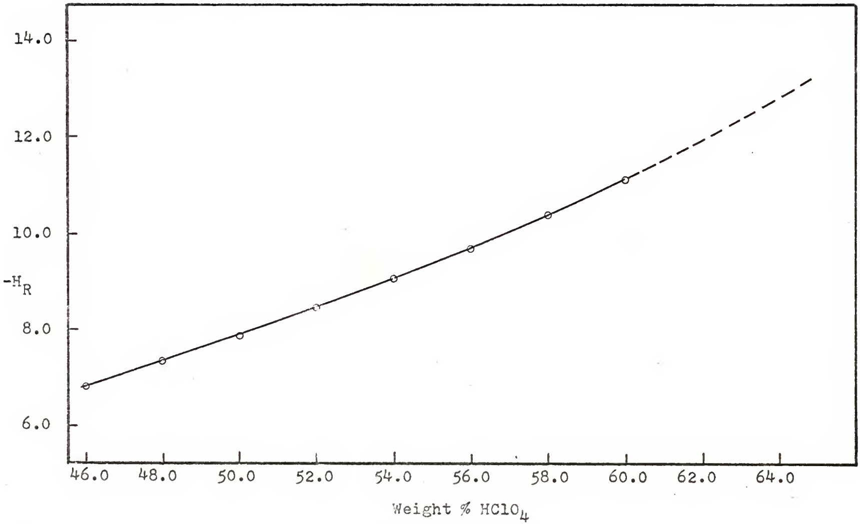


Fig. 20 .--Values of H_R in aqueous perchloric acid at 25°.

$$H_R = -pK_{HROH^{+1}} - \log C_{HR^{+2}}/C_{HROH^{+1}} \quad (13)$$

$$HROH^{+1} + H^{+} \xrightleftharpoons{K_{HROH^{+1}}} HR^{+2} + H_2O \quad (14)$$

λ_{max}; the concentration of $HROH^{+1}$ is seen to be equal to the difference between the expected Beer's Law absorbance and the absorbance measured at λ_{max} due to HR^{+2}. The expected Beer's Law absorbance is calculated by multiplying the initial absorbance observed at λ_{max} by the ratio of the initial volume to the actual volume after each dilution; referring to Appendix 1 it is seen that after the addition of ten drops of water this ratio has a value of 0.812.

For equal concentrations of HR^{+2} and $HROH^{+1}$ the $\log C_{HR^{+2}}/C_{HROH^{+1}} = 0$ and $pK_{HROH^{+1}} = -H_R$. In practice it may be impossible or impractical to effect equal concentrations by manipulating the acid strength and so, generally, values of this log term are calculated for points in the vicinity of this midpoint. In the present work such values were calculated for one or two points on either side of the midpoint and the corresponding $pK_{HROH^{+1}}$ values computed. The $pK_{HROH^{+1}}$ reported in Table 5 is the average of the $pK_{HROH^{+1}}$ values obtained in this manner (Table 5). Experimental points lying near the Beer's Law plot were not included in the calculations since they were found to give widely varying values of $pK_{HROH^{+1}}$, as compared with those points in the vicinity of the midpoint which gave consistently close $pK_{HROH^{+1}}$ values. Titration data collected for triphenylmethanol provide a check for the accuracy of the

TABLE 4

VALUES OF LOG Q[a] FOR ARYLMETHANOLS USED IN EVALUATING $pK_{HROH}{+1}$

Drop #	Dilution Fraction	$\%HClO_4$	$-H_R$	Log Q	$dH_R/d\log Q$	$pK_{HROH}{+1}$	$d\log Q/d\%HClO_4$
4,5-dimethyl-2-thiazolylbis(p-methoxyphenyl)methanol							
27	0.607	49.55	7.74	0.28		7.46	
					-1.17		0.23
28	0.597	49.04	7.60	0.16		7.44	
					-1.08		0.24
29	0.588	48.53	7.47	0.04		7.43	
					-1.08		0.27
30	0.580	48.04	7.33	-0.09		7.41	
4-methyl-2-thiazolylbis(p-methoxyphenyl)methanol							
23	0.646	51.71	8.35	0.36		7.99	
					-1.00		0.29
24	0.636	51.15	8.19	0.20		7.99	
					-1.07		0.27
25	0.625	50.60	8.03	0.05		7.98	
					-1.07		0.26
26	0.616	50.07	7.88	-0.09		7.98	
2,4-dimethyl-5-thiazolyldi(p-tolyl)methanol							
24	0.636	51.15	8.19	0.10		8.09	
					-1.33		0.22
25	0.625	50.06	8.03	-0.02		8.05	
					-0.94		0.30
26	0.616	50.07	7.88	-0.18		8.06	

TABLE 4 -- Continued

Drop #	Dilution Fraction	%$HClO_4$	$-H_R$	Log Q	dH_R/dlog Q	$pK_{HROH}+1$	dlog Q/d%$HClO_4$
2,3,4-trimethyl-5-(hydroxydi(p-tolyl)methyl)thiazolium iodide							
22	0.657	52.28	8.53	0.21		8.32	
					-1.13		0.28
23	0.646	51.71	8.35	0.05		8.30	
					-1.00		0.29
24	0.636	51.15	8.19	-0.11		8.30	
					-1.07		0.27
25	0.625	50.60	8.03	-0.26		8.29	
					-1.00		0.28
26	0.616	50.07	7.88	-0.41		8.29	
2-thiazolylbis(p-methoxyphenyl)methanol							
21	0.667	52.86	8.72	0.13		8.59	
					-1.12		0.29
22	0.657	52.28	8.53	-0.04		8.57	
					-1.13		0.28
23	0.646	51.71	8.35	-0.20		8.55	
					-1.07		0.27
24	0.636	51.15	8.19	-0.35		8.54	
4-pyridyldi(p-tolyl)methanol							
9	0.828	61.01	11.55	0.69		10.86	
					-0.88		0.44
10	0.812	60.24	11.25	0.34		10.91	
					-1.07		0.39
11	0.796	59.48	10.93	0.04		10.90	

TABLE 4 -- Continued

Drop #	Dilution Fraction	$\%HClO_4$	$-H_R$	Log Q	dH_R/dlog Q	$pK_{HROH}+1$	dlog Q/d$\%HClO_4$
12	0.782	58.75	10.64	-0.26	-0.97	10.90	0.41
4,5-dimethyl-2-thiazolyldi(p-tolyl)methanol							
9	0.828	61.01	11.55	0.45		11.10	
10	0.812	60.24	11.25	0.12	-0.91	11.13	0.43
11	0.796	59.48	10.93	-0.19	-1.03	11.12	0.41
12	0.782	58.75	10.64	-0.47	-1.04	11.11	0.38
2,4-dimethyl-5-thiazolyldi(p-tolyl)methanol							
9	0.828	61.01	11.55	0.31		11.24	
10	0.812	60.24	11.25	-0.03	-0.88	11.28	0.44
11	0.796	59.48	10.93	-0.35	-1.00	11.28	0.42
12	0.782	58.75	10.64	-0.65	-0.97	11.29	0.41
4-methyl-2-thiazolyldi(p-tolyl)methanol							
6	0.879	63.46	12.61	0.66		11.95	

TABLE 4 -- Continued

Drop #	Dilution Fraction	$\%HClO_4$	$-H_R$	Log Q	$dH_R/d\log Q$	$pK_{HROH}+1$	$d\log Q/d\%HClO_4$
					-1.06		0.43
7	0.861	62.62	12.23	0.30		11.93	
					-0.97		0.44
8	0.845	61.81	11.88	-0.06		11.94	
					-0.92		0.45
9	0.828	61.01	11.55	-0.42		11.97	
					-0.86		0.45
10	0.812	60.24	11.25	-0.77		12.02	
2-thiazolyldi(p-tolyl)methanol							
5	0.898	64.32	13.01	0.40		12.61	
					-0.98		0.48
6	0.879	63.46	12.61	-0.01		12.62	
					-0.95		0.48
7	0.861	62.62	12.23	-0.41		12.64	
triphenylmethanol							
26	0.616	50.07	7.88	0.75		7.13	
					-1.08		0.25
27	0.607	49.55	7.74	0.62		7.12	
					-1.27		0.21
28	0.597	49.04	7.60	0.51		7.09	

TABLE 4 -- Continued

Drop #	Dilution Fraction	$\%HClO_4$	$-H_R$	Log Q	$dH_R/d\log Q$	$pK_{HROH^{+1}}$	$d\log Q/d\%HClO_4$
2,4-dimethyl-5-thiazolylbis(p-methoxyphenyl)methanol							
15	0.734	36.78	4.93	0.21		4.72	
					-1.13		0.16
16	0.721	36.27	4.84	0.13		4.71	
					-1.29		0.14
17	0.709	35.78	4.75	0.06		4.69	

[a] $Q = C_{HR^{+2}}/C_{HROH^{+1}}$

TABLE 5

EQUILIBRIUM CONSTANTS ($pK_{HROH^{+1}}$ VALUES) AND STANDARD FREE ENERGIES OF FORMATION OF CARBONIUM IONS FROM TRIARYLMETHANOLS IN PERCHLORIC ACID AT 25°

$(HROH^{+1} + H^{+1} = HR^{+2} + H_2O)$

Triarylmethanol	$pK_{HROH^{+1}}$	ΔG^{o}(kcal mole^{-1})
2,4-dimethyl-5-thiazolylbis(p-methoxyphenyl)methanol	4.71	6.41
triphenylmethanol[a]	7.13[b]	9.70
4,5-dimethyl-2-thiazolylbis(p-methoxyphenyl)methanol	7.44	10.12
4-methyl-2-thiazolylbis(p-methoxyphenyl)methanol	7.99	10.87
2,4-dimethyl-5-thiazolyldi(p-tolyl)methanol	8.07	10.98
2,3,4-trimethyl-5-(hydroxydi(p-tolyl)methyl)thiazolium iodide	8.30	11.29
2-thiazolylbis(p-methoxyphenyl)methanol	8.56	11.64
4-pyridyldi(p-tolyl)methanol	10.89	14.81
4,5-dimethyl-2-thiazolyldi(p-tolyl)methanol	11.12	15.12
2,4-dimethyl-5-thiazolyldiphenylmethanol	11.27	15.33
4-methyl-2-thiazolyldi(p-tolyl)methanol	11.96	16.27
2-thiazolyldi(p-tolyl)methanol	12.62	17.16

[a]The equilibrium is $ROH + H^{+1} = R^{+1} + H_2O$.

[b]The $pK_{ROH} = 6.89$; $\Delta G = 9.37$, Deno et al. (45).

TABLE 6

EQUILIBRIUM CONSTANTS AND FREE ENERGIES OF FORMING CARBONIUM IONS FROM ARYLMETHANOLS AT 25°

Arylmethanol	Perchloric Acid[a]		Sulfuric Acid[b]	
	pK	ΔG	pK	ΔG
Triphenylmethanol	6.89	9.37	6.63	9.03
-4,4',4"-trisdimethylamino	-	-	-9.36	-12.73[c]
-4,4',4"-tristrimethylamino	-	-	15.16	20.62[d]
-4,4'-bisdimethylamino	-	-	-6.90	-9.38[c]
-4,4'-bistrimethylamino	-	-	12.04	16.37[d]
-4,4'-dimethyl[e]	-	-	-	-
-4,4'-dimethoxy	1.14	1.55	1.24	1.69
-4-nitro	9.76	13.27	9.15	12.44
Diphenylmethanol	-	-	13.1	17.8
-4,4'dimethyl	-	-	10.4	14.2
-4,4'-dimethoxy	-	-	5.71	7.78
2-Thienyldiphenylmethanol	-	-	3.4	4.6[f]
2-Thienylphenylmethanol	-	-	9.9	13.5[f]

[a]Taken from Deno et al. (45).

[b]Values not footnoted in this column are taken from Deno et al. (8).

[c]Goldacre and Phillips (46).

[d]Williams et al. (47).

[e]In aqueous HCl, pK_{ROH} for 4,4'-dimethyltriphenylmethanol = 4.71; ΔG = 6.41, Epple et al. (48).

[f]Pettit et al. (49).

TABLE 7

VALUES OF LOG Q FOR COMPLEXED

ARYLMETHANOLS -- $PdCl_2(ROH)_2$ -- USED IN EVALUATING $pK_{Pd(ROH)_2}$

Drop #	Dilution Fraction	$\%HClO_4$	$-H_R$	Log Q[a]	$dH_R/d\log Q$	$pK_{Pd(ROH)_2}$	$d\log Q/d\%HClO_4$
ROH = 2-thiazolylbis(p-methoxyphenyl)methanol							
23	0.646	51.71	8.35	0.10		8.25	
					-1.07		0.27
24	0.636	51.15	8.19	-0.05		8.24	
					-1.14		0.25
25	0.625	50.60	8.03	-0.19		8.22	
ROH = 4-pyridyldi(p-tolyl)methanol							
12	0.782	58.75	10.64	0.84		9.80	
					-1.04		0.35
13	0.767	58.03	10.38	0.59		9.79	
					-0.93		0.40
14	0.753	57.33	10.12	0.31		9.81	
ROH = 4,5-dimethyl-2-thiazolyldi(p-tolyl)methanol							
13	0.767	58.03	10.38	-0.04		10.42	
					-1.73		0.21
14	0.753	57.33	10.12	-0.19		10.31	
					-1.53		0.22
15	0.740	56.64	9.89	-0.34		10.23	
ROH = 2,4-dimethyl-5-thiazolyldiphenylmethanol							
18	0.702	54.69	9.26	0.11		9.15	

TABLE 7 -- Continued

Drop #	Dilution Fraction	$\%HClO_4$	$-H_R$	Log Q	$dH_R/d\log Q$	$pK_{Pd(ROH)_2}$	$d\log Q/d\%HClO_4$
					-1.11		0.29
19	0.690	54.06	9.06	-0.07		9.13	
					-0.82		0.36
20	0.679	53.45	8.88	-0.29		9.17	
ROH = 4-methyl-2-thiazolyldi(p-tolyl)methanol[b]							
13	0.767	58.03	10.38	0.27		10.11	
					-1.30		0.29
14	0.753	57.33	10.12	0.07		10.05	
ROH = 4-methyl-2-thiazolyldi(p-tolyl)methanol							
11	0.796	59.48	10.93	0.02		10.91	
					-1.45		0.27
12	0.782	58.75	10.64	-0.18		10.82	
					-0.87		0.42
13	0.767	58.03	10.38	-0.48		10.87	
ROH = 2-thiazolyldi(p-tolyl)methanol							
6	0.879	63.46	12.61	0.51		12.10	
					-0.90		0.50
7	0.861	62.62	12.23	0.09		12.14	
					-0.85		0.49
8	0.845	61.81	11.88	-0.32		12.20	

[a] $Q = C_{PdCl_2(ROH)R^{+}}{}^{1}/C_{PdCl_2(ROH)_2}$

[b] $PdBr_2(ROH)_2$

TABLE 8

EQUILIBRIUM CONSTANTS ($pK_{Pd(ROH)_2}$ VALUES) AND STANDARD FREE ENERGIES OF FORMATION OF CARBONIUM IONS FROM COMPLEXED TRIARYLMETHANOLS IN PERCHLORIC ACID

$$PdCl_2(ROH)_2 + H^{+1} = PdCl_2R(ROH)^{+1} + H_2O$$

Triarylmethanol	$pK_{Pd(ROH)_2}$	ΔG^o (kcal mole^{-1})
2-thiazolylbis(*p*-methoxyphenyl)methanol	8.24	11.21
4-pyridyldi(*p*-tolyl)methanol	9.80	13.33
4,5-dimethyl-2-thiazolyldi(*p*-tolyl)methanol	10.31	14.02
2,4-dimethyl-5-thiazolyldiphenyl methanol	9.15	12.44
4-methyl-2-thiazolyldi(*p*-tolyl)methanol[a]	10.08	13.71
4-methyl-2-thiazolyldi(*p*-tolyl)methanol	10.87	14.78
2-thiazolyldi(*p*-tolyl)methanol	12.14	16.51

[a] $PdBr_2(ROH)_2$

experimental technique employed; the dilution curve is shown in Figure 43.

The titration data for the complexed cations were handled in a manner analogous to that for the free cations. The interpretation of the dilution curves in terms of the species involved is contained in the Discussion Section. The dilution curves for related pairs of carbonium ions -- free and complexed -- follow in sequential order in Figures 21-42 .

Proton Magnetic Resonance Spectra

The pmr spectra for the ligands, obtained at 60 MHz in deuterochloroform and using TMS as the internal standard, are reported in Table 9. The characteristic features noted in the pmr spectra of these compounds are summarized below:

1. In the spectra of the 2-thiazolyl series coupling between the protons in the 4- and 5-positions on the thiazole ring is observed with a coupling constant of 3.3 cps.

2. In the spectra of the 4-methyl-2-thiazolyl series coupling between the methyl group in the 4-position and the proton in the 5-position on the thiazole ring is observed. The resulting quartet and doublet display a coupling constant of 1.0 cps.

3. In the spectra of the 4,5-dimethyl-2-thiazolyl series no coupling between the methyl groups in the 4- and 5-positions on the thiazole ring is observed. The expected singlets appear as a single peak in the pmr spectra due to an accidental degeneracy.

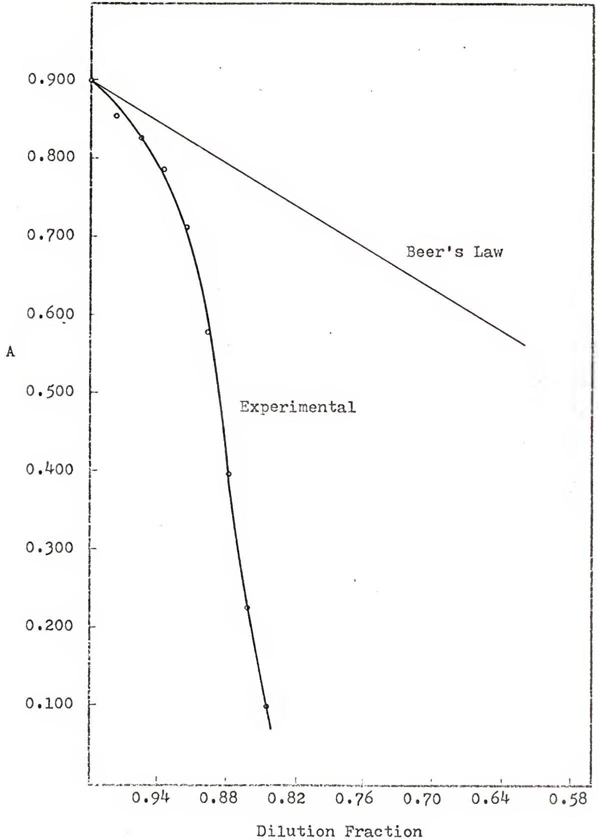


Fig. 21.--Dilution curves for 2-thiazolyldi(p-tolyl)methanol.

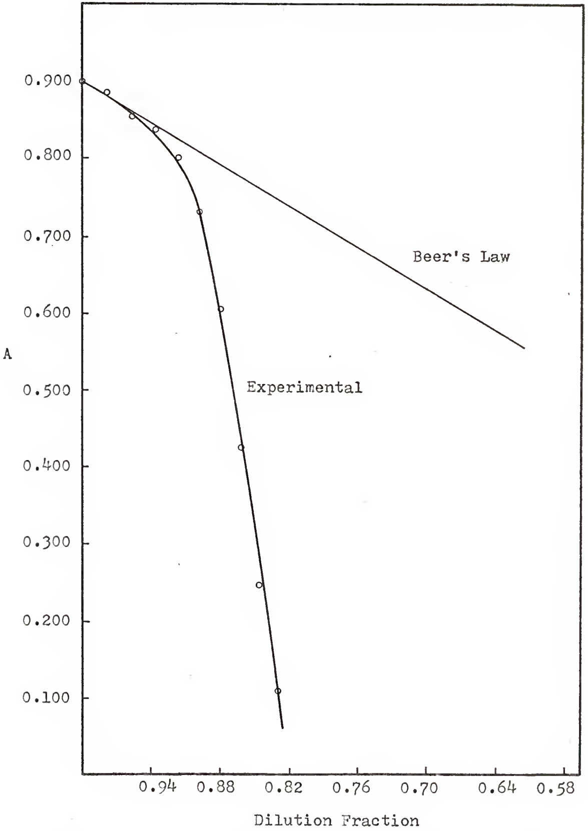


Fig. 22.--Dilution curves for the dichloropalladium(II) complex of 2-thiazolyldi(p-tolyl)methanol.

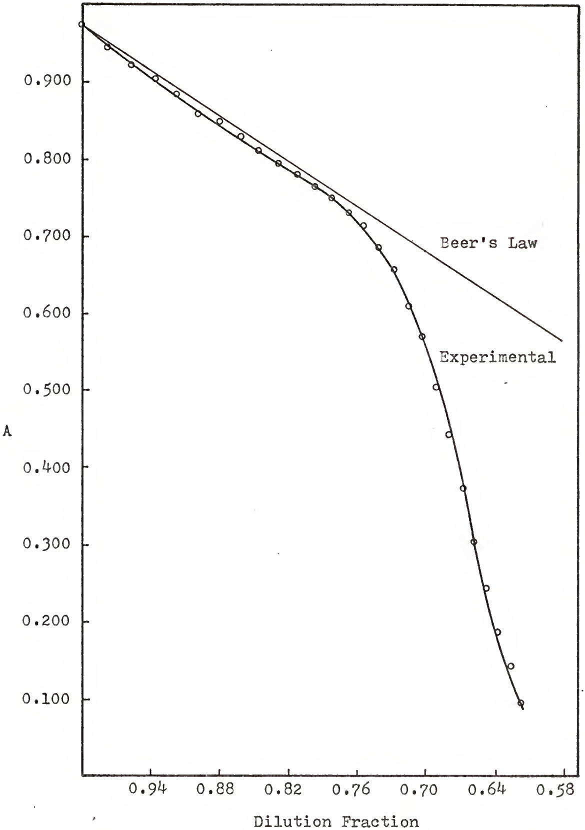


Fig. 23.--Dilution curves for 2-thiazolylbis(p-methoxyphenyl)methanol.

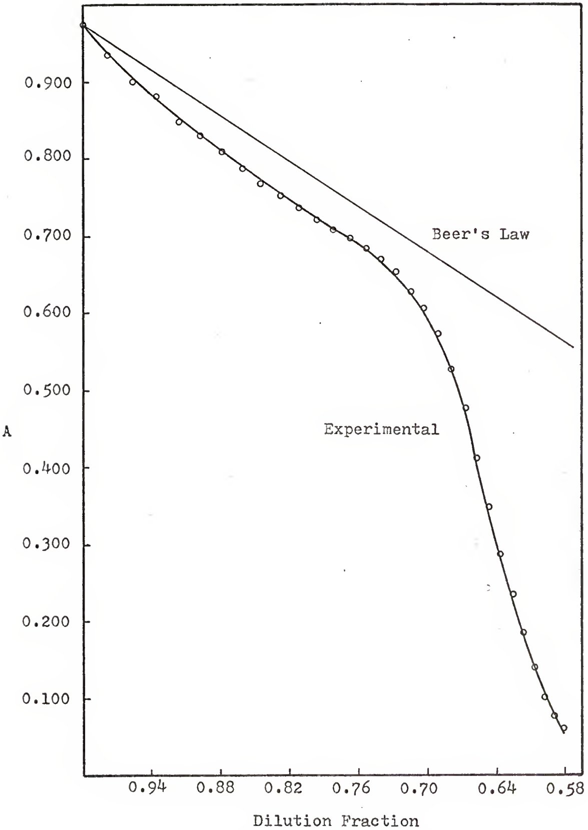


Fig. 24.--Dilution curves for the dichloropalladium(II) complex of 2-thiazolylbis(p-methoxyphenyl)methanol.

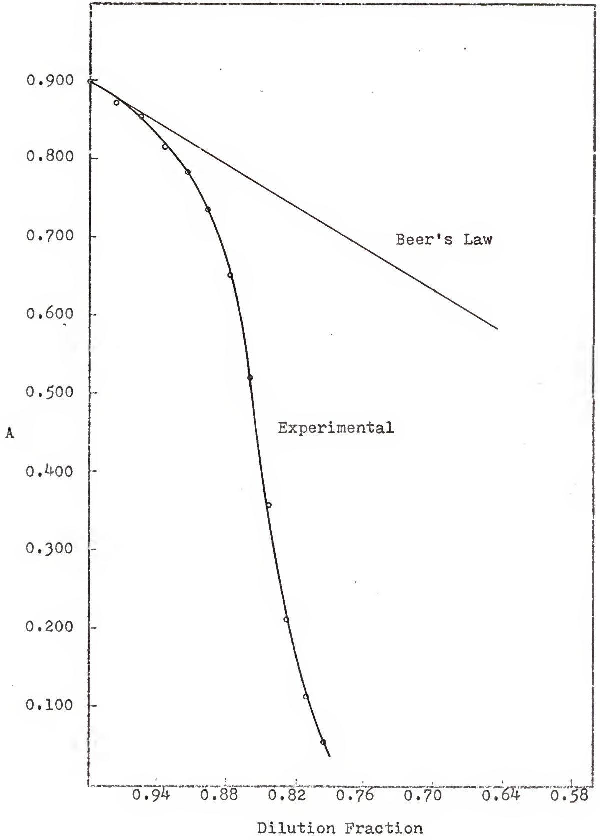


Fig. 25.--Dilution curves for 4-methyl-2-thiazolyldi-(p-tolyl)methanol.

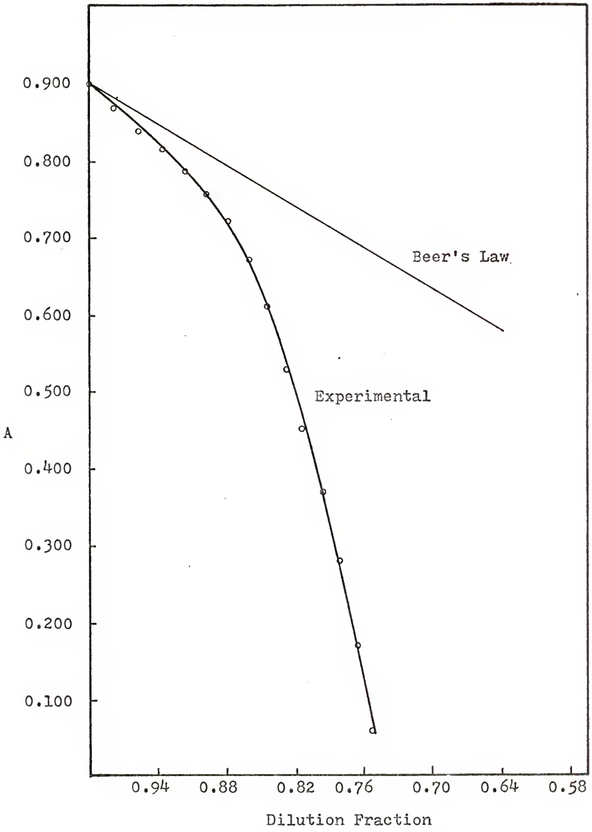


Fig. 26.--Dilution curves for the dichloropalladium(II) complex of 4-methyl-2-thiazolyldi(p-tolyl)methanol.

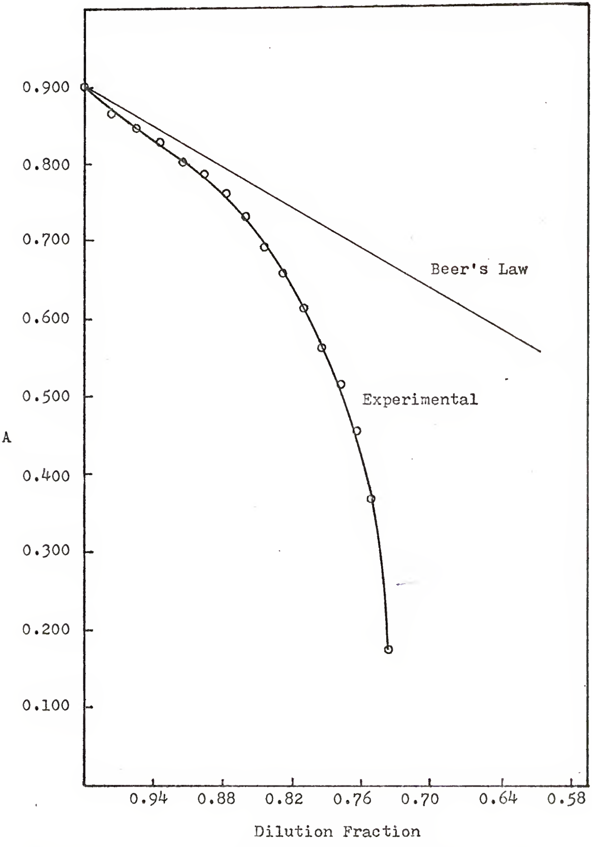


Fig. 27 .--Dilution curves for the dibromopalladium(II) complex of 4-methyl-2-thiazolyldi(p-tolyl)methanol.

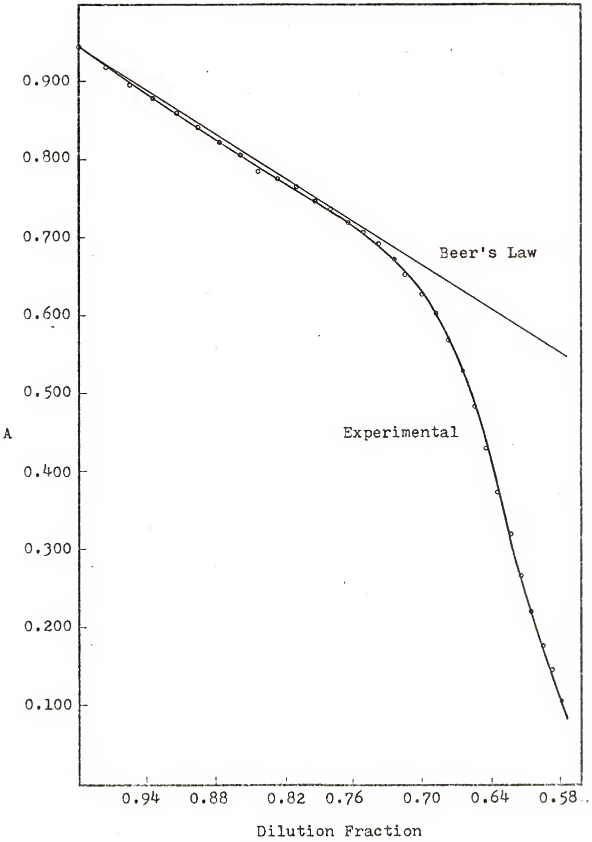


Fig. 28.--Dilution curves for 4-methyl-2-thiazolylbis-(p-methoxyphenyl)methanol.

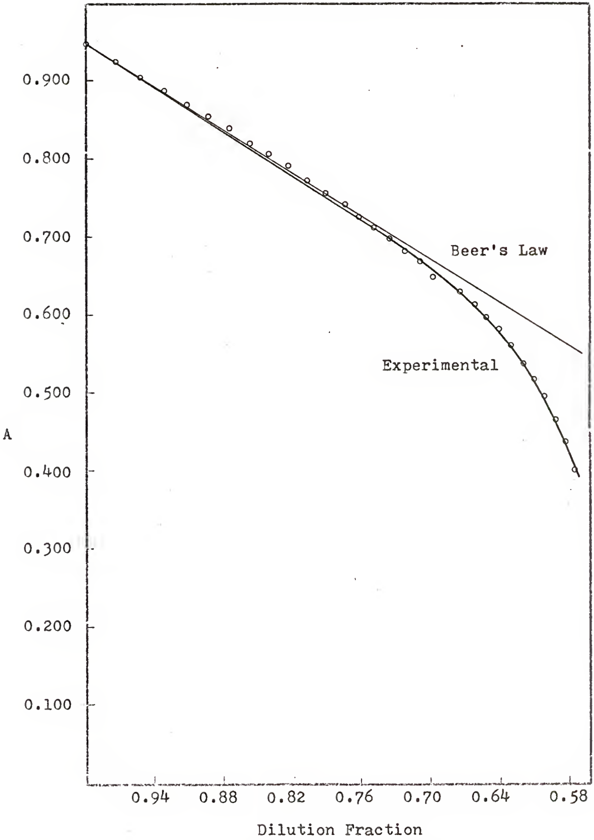


Fig. 29.--Dilution curves for the dichloropalladium(II) complex of 4-methyl-2-thiazolylbis(p-methoxyphenyl)methanol.

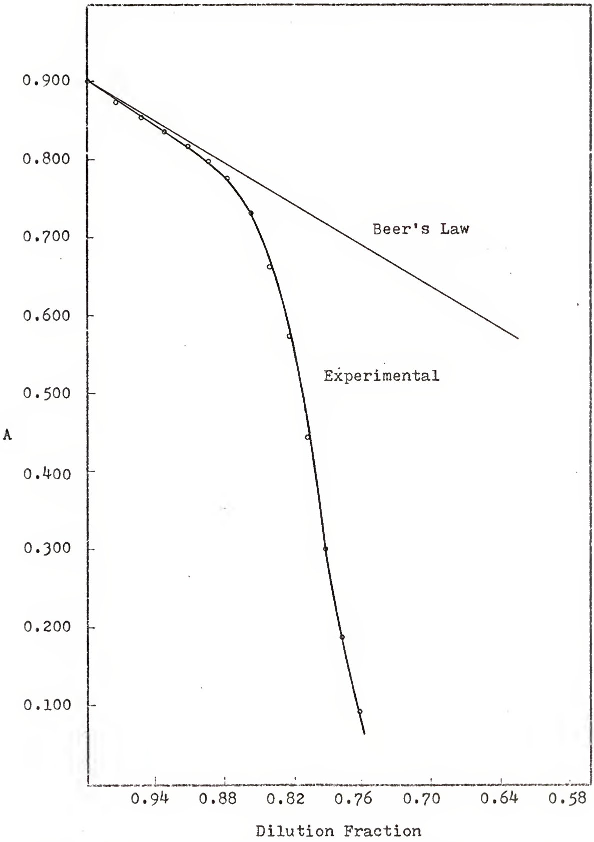


Fig. 30.--Dilution curves for 4,5-dimethyl-2-thiazolyl-di(p-tolyl)methanol.

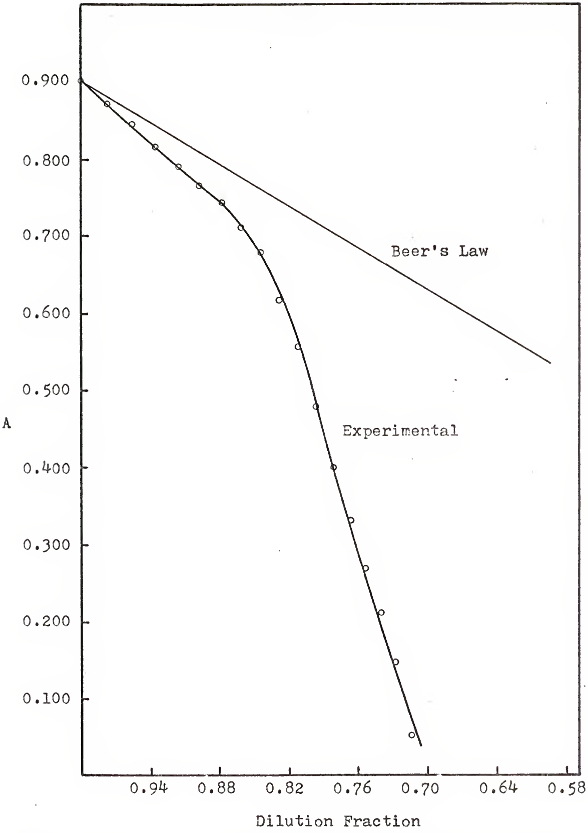


Fig. 31.--Dilution curves for the dichloropalladium(II) complex of 4,5-dimethyl-2-thiazolyldi(p-tolyl)-methanol.

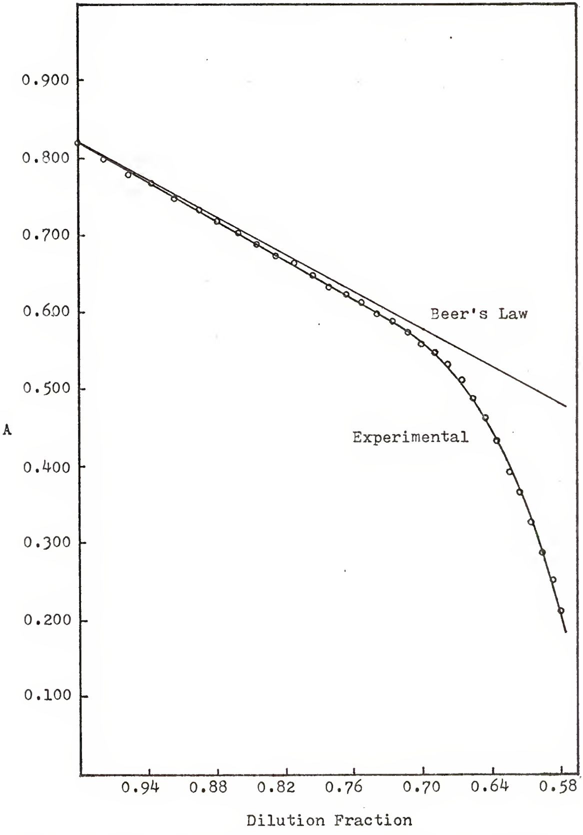


Fig. 32.--Dilution curves for 4,5-dimethyl-2-thiazolyl-bis(p-methoxyphenyl)methanol.

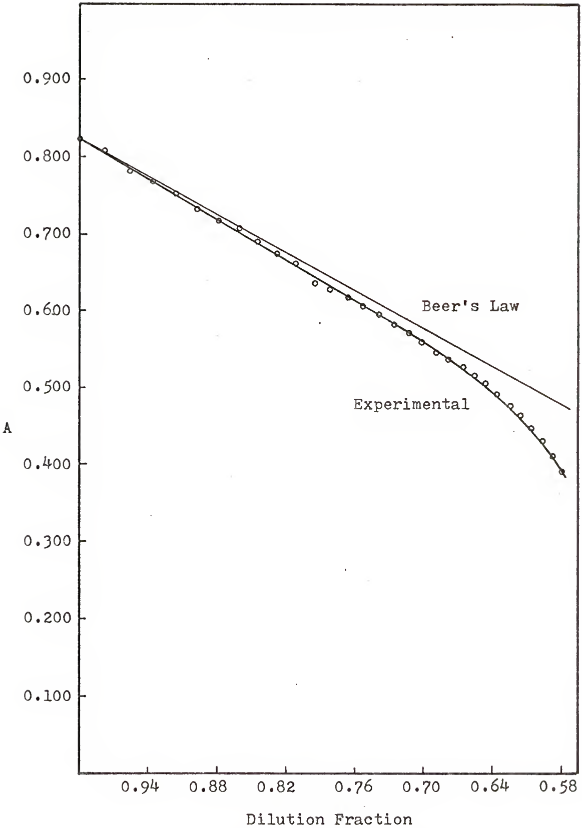


Fig. 33.--Dilution curves for the dichloropalladium(II) complex of 4,5-dimethyl-2-thiazolylbis(p-methoxyphenyl)methanol.

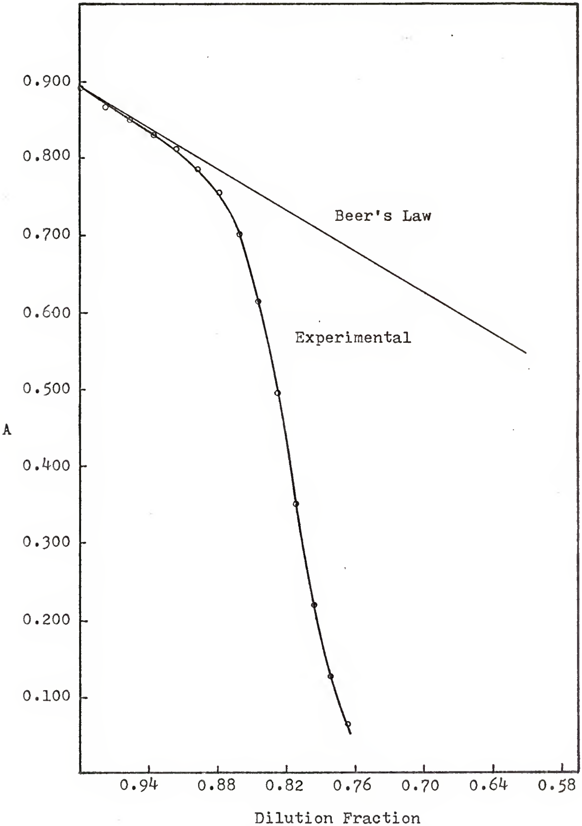


Fig. 34 .--Dilution curves for 2,4-dimethyl-5-thiazolyl-diphenylmethanol.

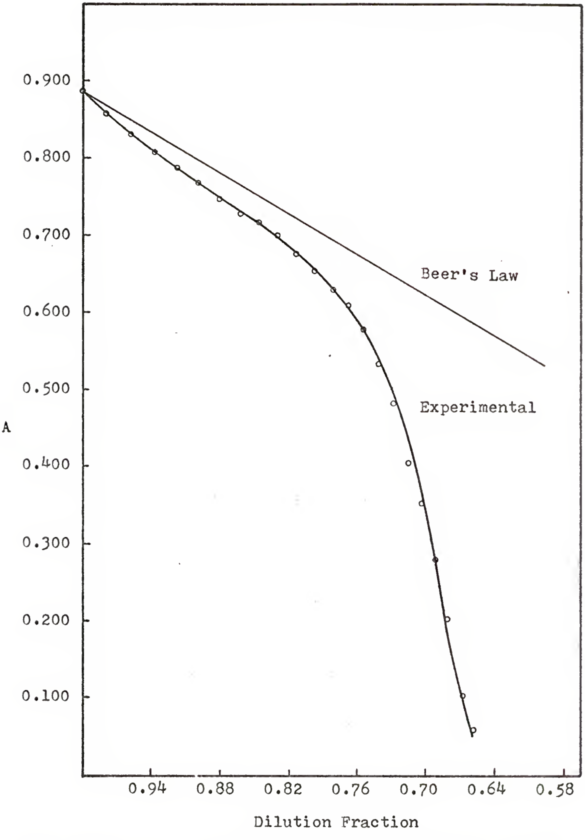


Fig. 35.--Dilution curves for the dichloropalladium(II) complex of 2,4-dimethyl-5-thiazolyldiphenylmethanol.

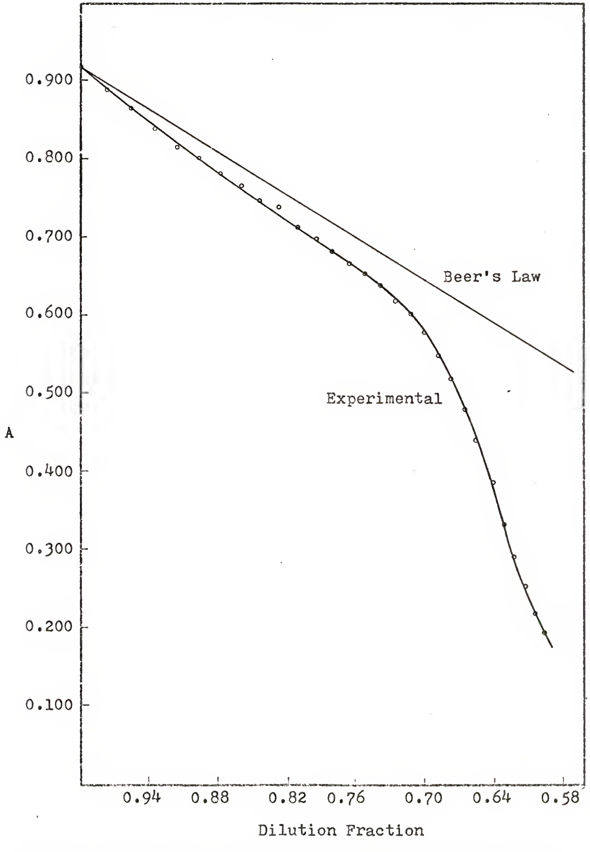


Fig. 36.--Dilution curves for 2,4-dimethyl-5-thiazolyl-di(p-tolyl)methanol.

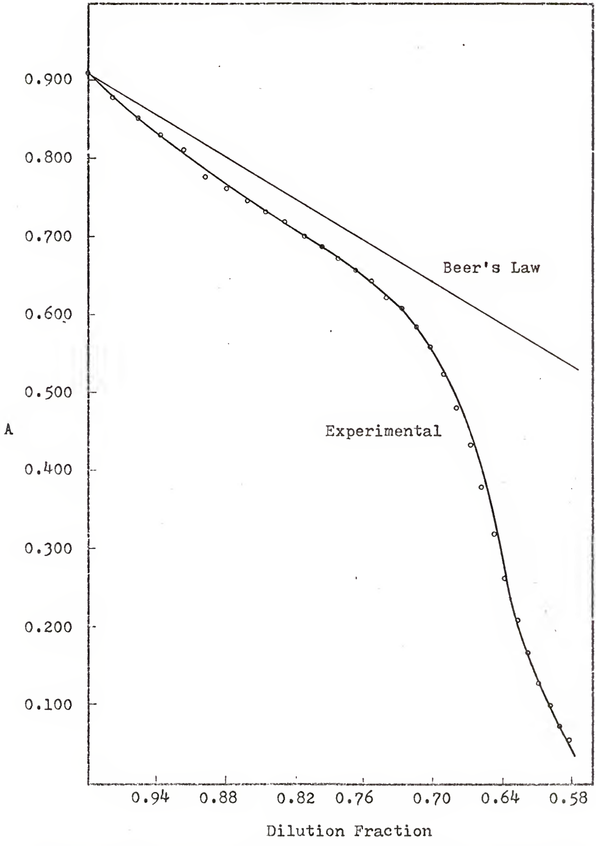


Fig. 37.--Dilution curves for 2,3,4-trimethyl-5-(hydroxy-di(p-tolyl)methyl) thiazolium iodide.

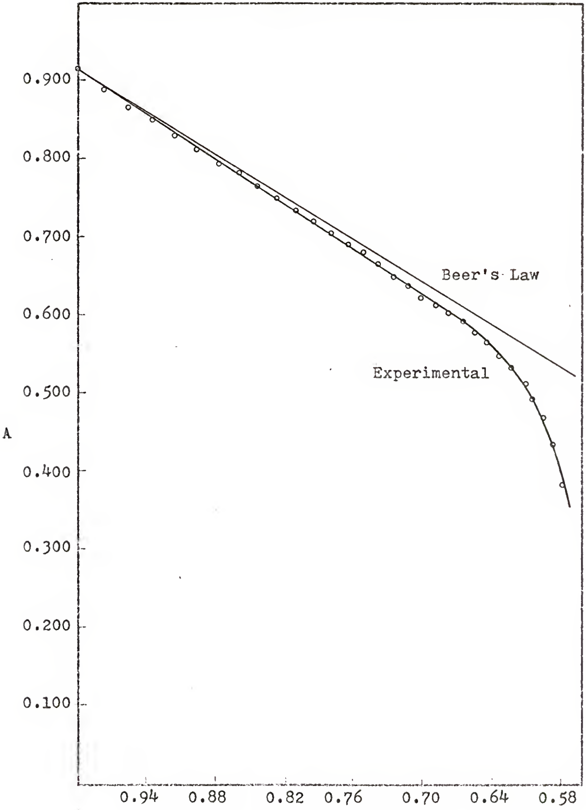


Fig. 38--Dilution curves for the dichloropalladium(II) complex of 2,4-dimethyl-5-thiazolyldi(p-tolyl)-methanol.

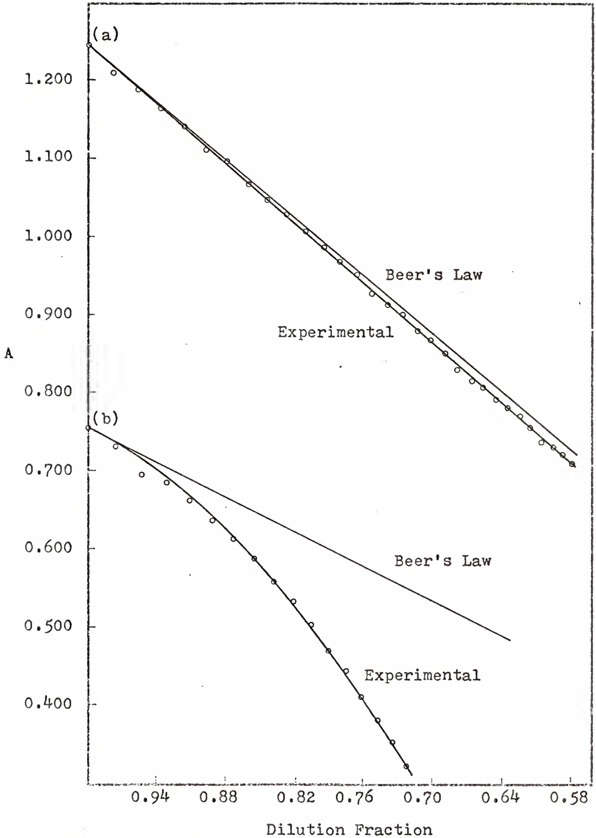


Fig. 39 .--Dilution curves for 2,4-dimethyl-5-thiazolyl-bis(p-methoxyphenyl)methanol.

(a) 69% $HClO_4$
(b) 46% $HClO_4$

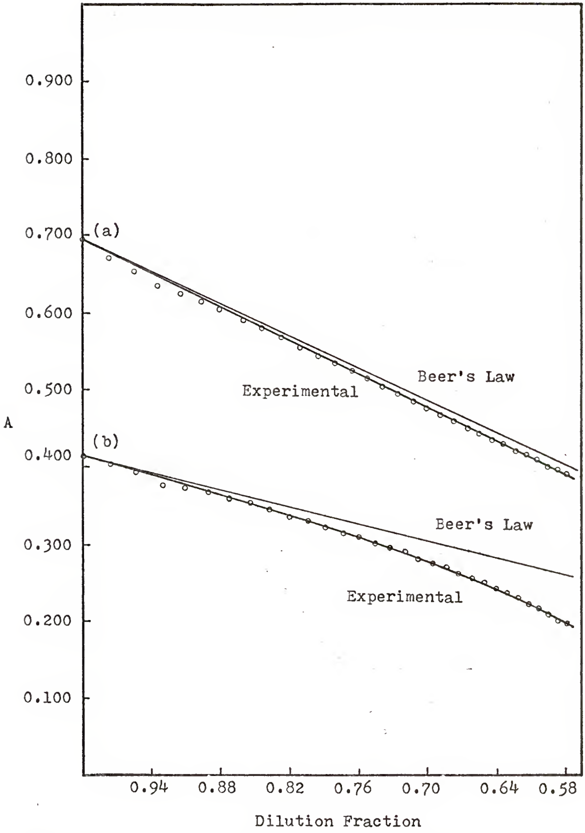


Fig. 40.--Dilution curves for the dichloropalladium(II) complex of 2,4-dimethyl-5-thiazolylbis(*p*-methoxyphenyl)methanol.

(a) 69% $HClO_4$
(b) 46% $HClO_4$

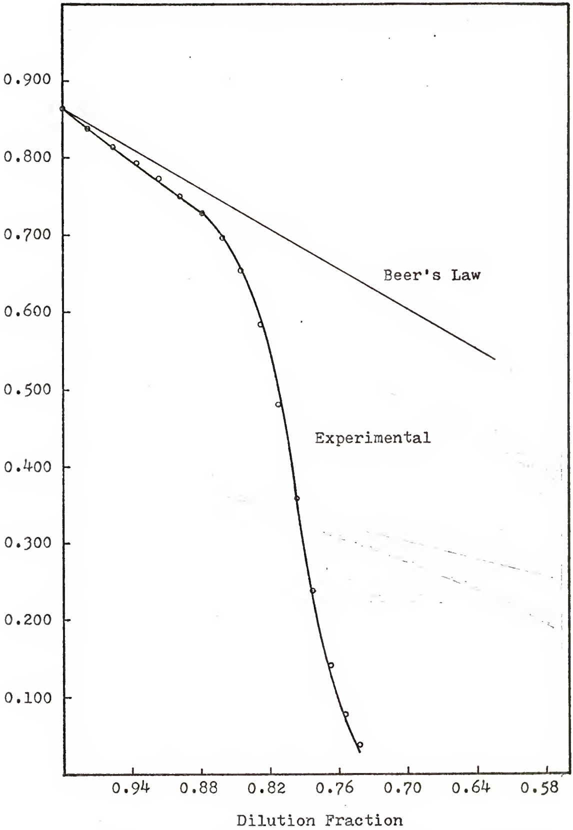


Fig. 41.--Dilution curves for 4-pyridyldi(p-tolyl)methanol.

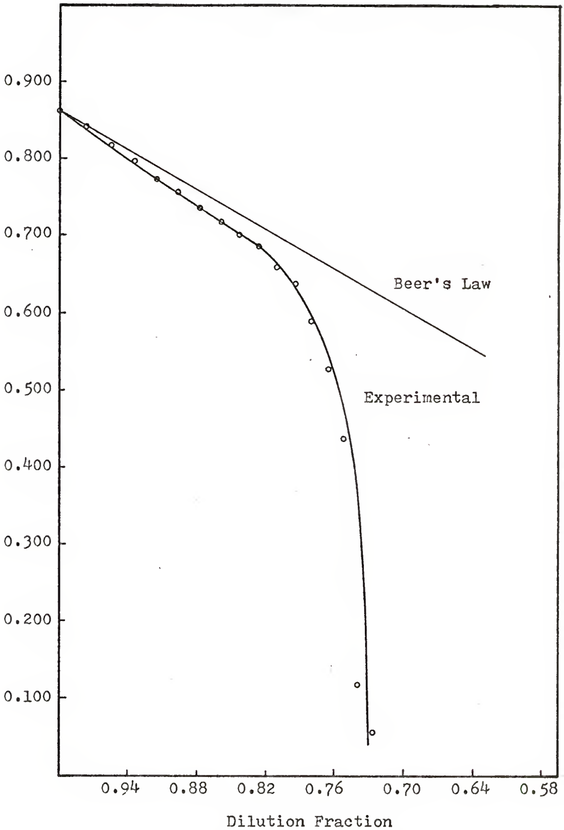


Fig. 42.--Dilution curves for the dichloropalladium(II) complex of 4-pyridyldi(p-tolyl)methanol.

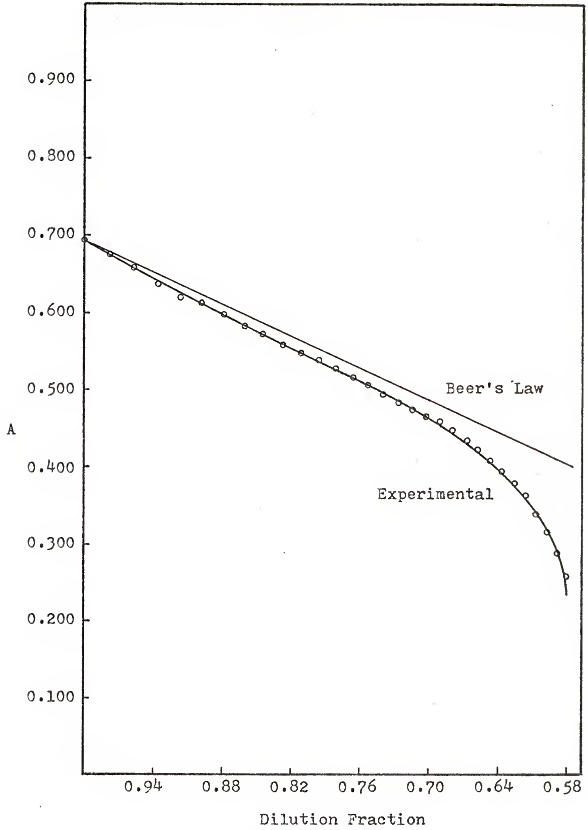


Fig. 43.--Dilution curves for triphenylmethanol.

The substitution of a methyl or methoxy group at the para-position of the benzene ring leads to the familiar A_2B_2 coupling pattern for the ring protons. Accepted convention places the A protons at the 2-position and the B protons at the 3-position. As the electron-releasing character of the para-substituent increases, the B proton resonance moves progressively upfield while the A proton resonance remains at the same field strength. This increases the chemical shift difference between the A and B protons and also results in an increase in the intensity of the outer pair of lines of the A_2B_2 pattern at the expense of the inner pair; for the limiting case of an A_2X_2 coupling pattern the inner and outer lines are of equal intensity.

Whereas the spectra of the ligands obtained in deuterochloroform were sharp and clearly defined the spectra of the corresponding carbonium ions obtained in perchloric acid were generally of lower quality with a tendency toward broadness and a lack of ringing. However, these same degenerate features were shown for the methyl resonances on the thiazole ring in the spectrum of the N-methyl iodide salt of 2,4-dimethyl-5-thiazolyldi(p-tolyl)methanol obtained in deuterochloroform. This suggests that these features may be due to charge effects.

The pmr spectra for each member of the 2,4-dimethyl-5-thiazolyl series were obtained in perchloric acid. For the other series only the para-methoxyphenyl members gave a stable pmr signal. The pmr spectra for 2-thiazolylbis-(p-methoxyphenyl)methanol and its corresponding carbonium

ion are presented in Figures 44 and 45 as typical of the quality of the spectra obtained. The phenyl and <u>para</u>-tolyl members did not give a pmr spectrum in perchloric acid. An exception was 4,5-dimethyl-2-thiazolyldi(<u>p</u>-tolyl)methanol which gave a signal for a freshly prepared solution run immediately but which broadened and disappeared completely within a few minutes. No solid was observed in the nmr tube and the reference signal remained stable. This behavior suggested that a free radical species was being generated and led to the epr experiments described subsequently.

The palladium complexes were not soluble in perchloric acid to the extent required for pmr spectroscopy and as a result no spectra were obtained for the complexed cations. The CAT was not employed because of the considerable length of time involved for a run and the fact that the complexes dissociate upon standing.

<u>Electron Paramagnetic Resonance Spectra</u>

Perchloric acid glasses of the phenyl and <u>para</u>-tolyl carbonium ions were scanned at liquid nitrogen temperature. An epr signal corresponding to g = 2.0 was observed in all cases and was characterized by a single line devoid of any hyperfine structure; the half widths were <u>ca.</u> 15 gauss. The first experiments were run at concentrations appropriate for pmr spectroscopy whereas much lower concentrations were used in later experiments.

Fig. 44--Pmr spectrum of 2-thiazolylbis(*p*-methoxyphenyl)-methanol in deuterochloroform.

Sweep width: 500 Hz

Peak positions (δ): 7.76, 7.25; 7.27, 6.81; 3.78

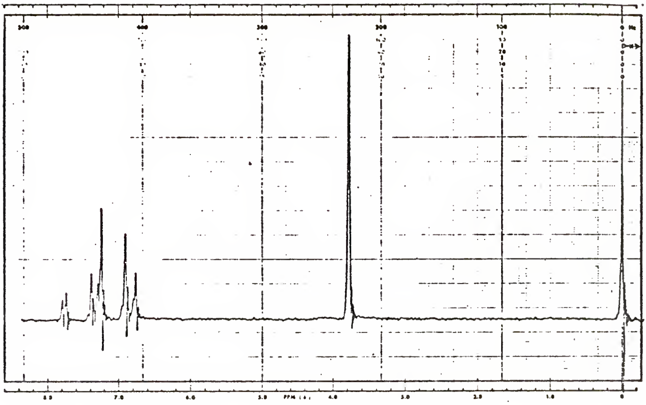
Internal standard: TMS (0.00δ)

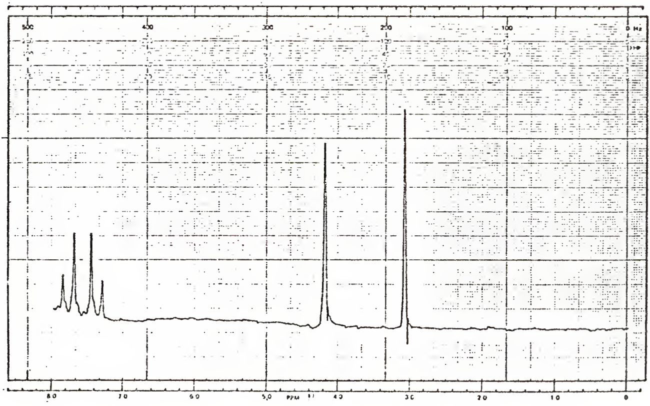
Fig. 45--Pmr spectrum of the 2-thiazolylbis(*p*-methoxyphenyl)methyl cation in perchloric acid.

Sweep width: 500 Hz

Peak positions (δ): 7.75, 7.41; 4.22

Internal standard: $NMe_4^+ BF_4^-$ (3.10δ)





The formation of the free radical is intimately related to the stability and concentration of the corresponding carbonium ion. That is, the tendency to form the free radical species increases as the stability of the carbonium ion decreases. As such this tendency is directly proportional to the electrophilicity of the cation. While none of the *para*-methoxyphenyl cations formed free radicals all of the *para*-tolyl and phenyl members of the 2-thiazolyl, 4-methyl-2-thiazolyl, and 4,5-dimethyl-2-thiazolyl series did. Formation of the radical was strikingly concentration dependent. A 1.5×10^{-2}*M* solution of the 4,5-dimethyl-2-thiazolyldiphenylmethyl cation gave an epr signal but, upon a ten-fold dilution,no signal could be observed. This behavior was displayed by each of the cations which gave radicals whereupon dilution wiped out the signal completely. This negated all attempts to observe hyperfine structure since at the higher concentrations for which a signal was observed the phenomenon of 'exchange narrowing' was most probably operative. This had the effect of masking any hyperfine structure by collapsing the epr signal into a single line.

TABLE 9

PMR CHEMICAL SHIFTS OF ARYLMETHANOLS IN DEUTEROCHLOROFORM

Arylmethanol	δ_{H_4}	δ_{H_5}	δ_{ϕ}	δ_{CH_3}	δ_{OCH_3}	δ_{CH_3I}
2-thiazolyldiphenylmethanol	7.75	7.27	7.23	-	-	-
-4,4'-dimethyl	7.75	7.25	7.25 7.11	2.33	-	-
-4,4'-dimethoxy	7.76	7.25	7.27 6.81	-	3.78	-
	δ_{4-CH_3}	δ_{H_5}	δ_{ϕ}	δ_{CH_3}	δ_{OCH_3}	δ_{CH_3I}
4-methyl-2-thiazolyldiphenylmethanol	2.43	6.83	7.33	-	-	-
-4,4'-dimethyl	2.39	6.78	7.26 7.09	2.32	-	-
-4,4'-dimethoxy	2.41	6.81	7.29 6.81	-	3.77	-
	δ_{4-CH_3}	δ_{5-CH_3}	δ_{ϕ}	δ_{CH_3}	δ_{OCH_3}	δ_{CH_3I}
4,5-dimethyl-2-thiazolyldiphenylmethanol	2.27	2.27	7.31	-	-	-
-4,4'-dimethyl	2.28	2.28	7.29 7.12	2.32	-	-
-4,4'-dimethoxy	2.25	2.25	7.28 6.80	-	3.73	-

TABLE 9 -- Continued

	$\delta_{2\text{-}CH_3}$	$\delta_{4\text{-}CH_3}$	δ_{ϕ}	δ_{CH_3}	δ_{OCH_3}	δ_{CH_3I}
2,4-dimethyl-5-thiazolyldiphenylmethanol	2.53	2.00	7.35	-	-	-
-4,4'-dimethyl	2.51	2.00	7.23 7.04	2.33	-	-
-4,4'-dimethyl, N-methyl iodide	2.92	2.25	7.29 7.13	2.32	-	3.97
-4,4'-dimethoxy	2.52	1.99	7.26 6.84	-	3.78	-

TABLE 10

PMR CHEMICAL SHIFTS OF CARBONIUM IONS IN PERCHLORIC ACID

Arylmethanol	δ_{H_4}	δ_{H_5}	$\delta_{\emptyset}$	δ_{OCH_3}	δ_{CH_3}
2-thiazolyldiphenylmethanol	-	-	-	-	-
-4,4'-dimethoxy	sm	sm	7.76 7.41	4.22	-
	$\delta_{4\text{-}CH_3}$	δ_{H_5}	$\delta_{\emptyset}$	δ_{OCH_3}	δ_{CH_3}
4-methyl-2-thiazolyldiphenylmethanol	-	-	-	-	-
-4,4'-dimethoxy	2.82	sm	7.79 7.38	4.17	-
	$\delta_{4\text{-}CH_3}$	$\delta_{5\text{-}CH_3}$	$\delta_{\emptyset}$	δ_{OCH_3}	δ_{CH_3}
4,5-dimethyl-2-thiazolyldiphenylmethanol	-	-	-	-	-
-4,4'-dimethyl	2.86	2.81	7.74	-	2.69
-4,4'-dimethoxy	2.76	2.71	7.78 7.36	4.17	-

TABLE 10 -- Continued

	$\delta_{2\text{-}CH_3}$	$\delta_{4\text{-}CH_3}$	$\delta_{\emptyset}$	δ_{OCH_3}	δ_{CH_3}
2,4-dimethyl-5-thiazolyldiphenylmethanol	3.23	2.32	7.88	-	-
-4,4'-dimethyl	3.17	2.32	7.67	-	2.81
-4,4'-dimethoxy	3.13	2.25	7.73 7.32	4.15	-

sm = solvent masked

DISCUSSION

Synthesis

The preparation of the 15 thiazolyl alcohols (ligands) reported herein involved reactions between the appropriate thiazolyllithium reagent and ketone. As such it represents the first systematic approach to the preparation of the triarylmethanols and ethanols described. Only two of these alcohols have been prepared previously, viz., 2-thiazolyldiphenylmethanol by Kurkjy and Brown (37) and by Metzger and Beraud (50), and 4,5-dimethyl-2-thiazolyldiphenylmethanol by Kurkjy and Brown (37). In the procedure as it was finally developed the reactions were all run at -70^{o} eliminating the side reactions which not only gave colored impurities but which seemed to make purification difficult. Simple hydrolysis of the reaction mixture using water proved to be a satisfactory route to the alcohols. For the phenyl and p-tolyl derivatives purification usually entailed a single recrystallization of the precipitated product. The p-methoxyphenyl derivatives often separated as oils which crystallized only after purification by column chromatography using alumina as the adsorbent packing. The yields were generally greater than 50 percent. The low yields that are reported were for reactions performed in the early stages

of the experimental work and reflect problems in technique which were subsequently overcome.

The reaction between n-butyl lithium and 2,4-dimethylthiazole followed by the addition of ketone led to a single product in which substitution had occurred exclusively on the 2-methyl group of 2,4-dimethylthiazole. It is interesting to note that Metzger and Beraud (50) have reported substitution to occur exclusively at the 5-position on the thiazole ring for the reaction between this lithium derivative and acetaldehyde at -60°. In a later paper Metzger and Crousier (51) indicated that a mixture of the 5-substituted and 2-methyl substituted products resulted in relative proportions dependent on the reaction and hydrolysis temperatures.

Visible Spectra

The visible absorption spectra of the cations -- free and complexed -- are best discussed in terms of the general characteristics and trends observed, viz.,

1. The cations are intensely colored with ϵ_{max} of ca. 10^4.

2. The p-tolyl and p-methoxyphenyl cations exhibit two absorptions in the visible region whereas the phenyl cations exhibit only one broad absorption. (An exception is encountered in the case of the 2-thiazolyldiphenylmethyl cation which has two characteristic absorptions.) It is suggested that the one broad absorption characterizing some of the cations is comprised of two overlapping bands.

3. The lower energy absorption is always the more intense of the two.

4. Within each series of free cations the separation (in nanometers) between the two absorption bands increases as the <u>para</u>-substituent on the phenyl ring is changed from $-H$ to $-CH_3$ to $-OCH_3$. This arises as a consequence of a bathochromic shift of the low-energy absorption and a hypsochromic shift of the high-energy absorption.

5. The complexed cations show a decrease in the separation between the two absorption maxima when compared with the corresponding free cations. In fact the two absorptions overlap severely. This arises from a combination of bathochromic and hypsochromic shifts for the higher energy and lower energy absorptions, respectively.

6. The colors of the solutions of the more stable, complexed cations remain intense even after exposure to the atmosphere overnight; however, the visible spectra of these solutions revealed that the complex had dissociated, i.e., the spectra were those characteristic of the uncoordinated cations. It was determined, however, that dissociation of the complexes did not normally occur so rapidly that reliable physical measurements could not be completed. (No detectible dissociation occurs within a period of two hours.)

The molar absorptivities are of the same order of magnitude as those observed for the related trityl cations. This suggests that in 69 percent perchloric acid the methanols are completely (or nearly completely) ionized to the corresponding cations. The dilution curves provide

concrete support for this premise, especially for the more stable carbonium ions. That is, the extensive superposition of the experimental curve upon the Beer's Law plot corresponds to simple dilution, the value for the molar absorptivity remaining constant. It is this constancy which exists only for 100 percent ionization and as the two curves diverge there is an accompanying decrease in the apparent molar absorptivity. For the less stable carbonium ions this divergence commences early along the dilution curve and for the 2-thiazolyldi(p-tolyl)methyl cation there is little suggestion of any overlap at all. Thus, the molar absorptivity reported for this cation may well be too small (Table 2). In a similar manner it is reasonable to conclude that the phenylmethanols of the 2-thiazolyl, 4-methyl-2-thiazolyl, and 4,5-dimethyl-2-thiazolyl series are not completely converted to the corresponding cations in 69 percent perchloric acid. None the less, the fact that the absorptivities of these cations are ca. 10^4 suggests that the equilibria lie in favor of the cations although the balance could easily be shifted by the addition of a small amount of water. The fact remains that these cations are unsuitable for the dilution curve technique employed to obtain pK_{HROH^+1} values.

The H_R Acidity Function and Thermodynamic Stability

The thermodynamic stability of a carbonium ion R^{+1} may be defined in terms of the relative position of the equilibrium

$$ROH + H^{+1} = R^{+1} + H_2O \qquad (15)$$

and the magnitude of the equilibrium constant K_{ROH} where

$$K_{ROH} = a_{R^{+1}} a_{H_2O} / a_{ROH} a_{H^{+1}} \qquad (16)$$

and

$$pK_{ROH} = -\log a_{R^{+1}} a_{H_2O} / a_{ROH} a_{H^{+1}} \qquad (17)$$

expressed in terms of concentrations C and activity coefficients f the pK_{ROH} takes the form

$$pK_{ROH} = -\log C_{R^{+1}} f_{R^{+1}} C_{H_2O} f_{H_2O} / C_{ROH} f_{ROH} C_{H^{+1}} f_{H^{+1}} \qquad (18)$$

The value of pK_{ROH} pertains to the position of the equilibrium in some standard medium such as water. However, only for the strongest secondary base ROH is the extent of ionization in water large enough to detect spectroscopically whereas for a weak base ionization may be essentially complete only in a highly acidic solvent. Therefore, mixtures of water and acid are employed to generate measurable amounts of carbonium ion. The measurement of $C_{R^{+1}}/C_{ROH}$ usually depends on a difference in the electronic absorption spectra of the base and corresponding carbonium ion; these substances are often referred to as "indicators".

The evaluation of pK_{ROH} follows directly from knowledge of $C_{R^{+1}}/C_{ROH}$ as a function of acid concentration.

From the definition of pK_{ROH} it follows that at infinite dilution when all activity coefficients equal one

$$pK_{ROH} = -\log C_{R^{+}1}/C_{ROH} + \log C_{H^{+}1} \qquad (19)$$

Extrapolating to zero acid concentration a plot of pK_{ROH} versus acid concentration leads to the correct thermodynamic equilibrium constant pK_{ROH}. The linearity of this plot falls off as the acid concentration is increased (ca. 2M) with the extrapolation procedure ceasing to be reliable. Thus, the pK_{ROH} values for only the strongest secondary bases can be evaluated in this manner.

The non-linearity of the plots indicates that as the ionic strength of the medium increases, the ratio of the activity coefficients in equation (18) is no longer one, and the equilibrium expression written in terms of concentrations instead of activities is not valid. This led Deno and coworkers (8) to define an acidity function H_R, and to propose that H_R could be taken as a quantitative measure of the capacity of the medium to ionize an arylmethanol.

$$H_R = -pK_{ROH} - \log C_{R^{+}1}/C_{ROH} = -\log a_{H^{+}1} + \log a_{H_2O} + \log f_{R^{+}1}/f_{ROH} \qquad (20)$$

It follows that H_R will be independent of the particular indicator ROH used to measure it providing $f_{R^{+}1}/f_{ROH}$ is identical for all indicators in the same acid solution. This criterion may be demonstrated experimentally by taking two indicators R_1OH and R_2OH which ionize measurably in overlapping levels of acidity. The observed ionization

ratios will be related to the equilibrium constants by

$$pK_{R_1OH} - pK_{R_2OH} = -\log C_{R_1^{+1}}/C_{R_1OH} + \log C_{R_2^{+1}}/C_{R_2OH} + \log f_{R_1^{+1}}f_{R_2OH}/f_{R_1OH}f_{R_2^{+1}} \qquad (21)$$

If $f_{R_1^{+1}}/f_{R_1OH}$ and $f_{R_2^{+1}}/f_{R_2OH}$ are indeed identical then the last term in equation (21)drops out leaving

$$pK_{R_1OH} - pK_{R_2OH} = \log C_{R_2^{+1}}/C_{R_2OH} - \log C_{R_1^{+1}}/C_{R_1OH} \qquad (22)$$

Plots of $C_{R^{+1}}/C_{ROH}$ versus percent acid for both indicators should be parallel in the region where they overlap for H_R to be independent of the indicator, i.e., the slope dlog $(C_{R^{+1}}/C_{ROH})$/d%acid for each indicator should be equal in overlapping regions of acidity if equation (20)is to be valid.

In order to build up a table of H_R values it is necessary to have a sufficiently strong base R_1OH that its pK_{R_1OH} can be determined by extrapolating a plot of equation (19) versus percent acid to zero acid concentration. A weaker base R_2OH is then chosen for which $C_{R_2^{+1}}/C_{R_2OH}$ is measurable at the lower end of the acid concentration range which coincides with the higher end of the range over which $C_{R_1^{+1}}/C_{R_1OH}$ is measurable. This stepwise procedure is used to determine the pK_{ROH} values for successively weaker bases in increasingly acidic solutions.

The H_R acidity function is unique for the series of indicators used to evaluate it and is therefore different

from the Hammett H_0 acidity function, which measures the capacity of the medium to protonate a primary amine B.

$$B + H^{+1} = BH^{+1} \tag{23}$$

$$H_0 = -pK_B - \log C_{BH^{+1}}/C_B = -\log a_{H^{+1}} + \log f_{BH^{+1}}/f_B \tag{24}$$

The deviation between the H_R and H_0 acidity functions has been attributed mainly to the difference in the activity coefficients of the carbonium ion R^{+1} and the ammonium ion BH^{+1}. This difference has been rationalized by contrasting the solvation requirements and the effect upon solvent structure of these ions (52). Arnett and Bushick (53) suggest that carbonium ions undergo generalized dielectric solvation whereas ammonium ions undergo specific solvation effects through hydrogen bonding.

To establish whether or not a particular acidity function is appropriate for determining the pK of a particular base, the criterion that a plot of the log term involving the ratio of the concentrations of the acid and base forms of the indicator versus the acidity function be linear with slope -1.00 must be met. That is, it follows from equation (20) that the H_R acidity function is appropriate if a plot of the log $C_{R^{+1}}/C_{ROH}$ versus H_R is linear with slope -1.00.

Suitability of the H_R Acidity Function

The mechanics involved in applying the dilution curve data to the calculation of $pK_{HROH^{+1}}$ have been stated previously. Table 4 lists the values of H_R appropriate for each dilution and the values of log Q obtained from the spectral data; the calculation of $pK_{HROH^{+1}}$ follows from

$$pK_{HROH^{+1}} = -H_R - \log C_{HR^{+2}}/C_{HROH^{+1}} = -H_R + \log Q \quad (25)$$

Table 5 gives the average of the $pK_{HROH^{+1}}$ so obtained.

A plot of H_R versus log Q having a slope -1.00 would establish H_R as the acceptable acidity function. Rather than taking a graphical approach to determining the appropriateness of the H_R acidity function however $dH_R/d\log Q$ was evaluated between drops (Table 4). The general close proximity of $dH_R/d\log Q$ to -1.00 provides justification for using H_R. Note that even for triphenylmethanol $dH_R/d\log Q$ doesn't equal -1.00 exactly, but it is in accord with those values obtained for the heterocyclic bases investigated.

For equation (25) to be valid $d\log Q/d\%HClO_4$ for each indicator should be equal in overlapping regions of acidity. Table 4 suggests that this criterion has been met in general.

From equation (21) it is seen that H_R contains a contribution from a term involving the ratio of the activity coefficients of the two forms of the indicator. With H_R proving to be applicable in this work it then follows that $f_{R^{+1}}/f_{ROH} = f_{HR^{+2}}/f_{HROH^{+1}}$.

This type of behavior has been observed by Williams and co-workers (47) for the ionization of 4,4',4"-tris(dimethyl-

amino)triphenylmethanol and 4,4',4"-trinitrotriphenylmethanol in sulfuric acid. These two indicators ionized in overlapping levels of acid concentration (80-90 percent). The observed ionization ratios are related to the equilibrium constants by equation (22). In 80-90 percent sulfuric acid plots of log C_{R^+}/C_{ROH} for both indicators were essentially parallel. It is important to note that 4,4',4"-tris(dimethylamino)triphenylmethanol carries three integral units of positive charge in addition to the center of varying ionization whereas 4,4',4"-trinitrotriphenylmethanol becomes charged only at the central carbon atom. The reduction of equation (21) to equation (22) requires that $f_{R^{+4}}/f_{ROH^{+3}} = f_{R^{+1}}/f_{ROH}$. That is, within the limited region surveyed, it is unnecessary to distinguish between charge types. Deno and co-workers (8), however, have cast doubt on the generality of this simplification. The paucity of relevant information makes it impossible to evaluate any general applicability of Williams and co-workers' findings; however, in the present work there is little distinction between charge types.

Dilution Curves -- Free Cations

From a qualitative standpoint the dilution curves representing the electrophilicity of the carbonium ions toward water illustrate vividly the effect of different substituent groups on carbonium ion stability. The more effectual a group is in stabilizing a carbonium ion, the smaller the deviation between the Beer's Law and experi-

mental plots. Thus, from a visual comparison of the dilution curves one can order the carbonium ions according to their stability.

We are justified in approaching the evaluation of the dilution curves on a thermodynamic basis because it is the equilibrium between HR^{+2} and $HROH^{+1}$ which is being observed. This point was demonstrated by comparing the dilution curves of 2,4-dimethyl-5-thiazolyldi(p-tolyl)methanol and its N-methyl iodide salt. The two curves were essentially superimposable, in keeping with the assertion that the free cation is protonated.

The dilution curves for the more stable p-methoxyphenyl carbonium ions are virtually superimposable over extended dilutions, i.e., they correspond to a simple dilution of the solution containing HR^{+2} ion.

The H_R acidity function allowed the calculation of $pK_{HROH^{+1}}$ values for the equilibrium represented by equation (14). The standard free energy change for this transformation is predictably unfavorable; the values listed in Table 5 refer to the position of the equilibrium in water.

The dilution curves are presented with the least stable member of each series given first. In most cases, however, the phenyl member is not included due to gross instability which precluded employing the titration technique in the acidity range indicated.

The carbonium ion stability increases within each thiazolyl series as the <u>para</u>-substituent on the phenyl ring is changed from $-H$ to $-CH_3$ to $-OCH_3$ as evidenced by a com-

parison of the dilution curves. This is in accord with established trends within the trityl series of cations; the trend is customarily explained by invoking hyperconjugation effects for the stabilizing influence of $-CH_3$ and the more traditional concept of resonance effects, involving electron release for the stabilizing influence of $-OCH_3$.

Substitution of a methyl group at the 5- and/or 4-position of the thiazole ring stabilizes the 2-thiazolyl series of carbonium ions by ca. 1 kcal mole^{-1} per methyl group. It is reasonable to expect that for the 5-thiazolyl series the methyl groups at positions 2 and 4 of the thiazole ring would exert a similar stabilization. The difference of ca. 4 kcal mole^{-1} in the free energy of formation of the 4,5-dimethyl-2-thiazolyldi(p-tolyl)methyl cation and the 2,4-dimethyl-5-thiazolyldi(p-tolyl)methyl cation may then be rationalized from two viewpoints:

1. The inductive destabilization is less for the 5-thiazolyl cations because three bonds separate the cationic centers whereas the separation is only by two bonds for the 2-thiazolyl cations.

2. Molecular models indicate a possible "thru-space" repulsive interaction between the centers of positive charge for the 2-thiazolyl cations which is absent for the 5-thiazolyl series.

The 4-pyridyldi(p-tolyl)methyl cation and the trityl cation were included in order to compare the effects of a 4-pyridyl group and a phenyl group with the thiazolyl groups on the stability of otherwise identically substituted car-

bonium ions. The data for the 4-pyridyl carbonium ion and the 2-thiazolyldi(p-tolyl)methyl cation suggest that a 4-pyridyl-substituted cation is more stable by ca. 2 kcal mole^{-1} than a 2-thiazolyl-substituted cation; the closer proximity of the positive centers in the 2-thiazolyl cation accounts for the difference.

The free energies of formation for the trityl cation and the 2,4-dimethyl-5-thiazolyldiphenylmethyl cation indicate that a phenyl-substituted cation is ca. 5 kcal mole^{-1} more stable than a 2,4-dimethyl-5-thiazolyl-substituted cation. Among the thiazolyl groups investigated this one destabilizes the carbonium ion to the least extent relative to a phenyl-substituted carbonium ion. The word destabilizes is emphasized to again point out that protonation of the thiazole ring leads to energetically unfavorable di-positive carbonium ions.

In order of increasing stability the groups may be arranged: 2-thiazolyl < 4-methyl-2-thiazolyl < 4,5-dimethyl-2-thiazolyl ≤ 4-pyridyl < 2,4-dimethyl-5-thiazolyl < phenyl.

Previous investigations into the chemistry of heteroaromatic carbonium ions provide an interesting prelude to this work. Smith and Holley (54) determined the van't Hoff i factor equal to 5.00 and 4.90 for the ionization in 100 percent sulfuric acid of 2-pyridyl and 4-pyridyldiphenylmethanol, respectively. Complete ionization according to the stoichiometry

$$(C_6H_5)_2(C_5H_4N)COH + 3H_2SO_4 = (C_6H_5)_2(C_5H_4NH)C^{+2} + H_3O^{+1} + 3HSO_4^{-1} \quad (26)$$

requires i = 5.00. Titration experiments indicated the minimum weight percent of sulfuric acid necessary to produce the characteristic color of the cations. These values ranged from 66.0 and 56.5 for the 2-pyridyl and 4-pyridyldiphenylmethanols to 72.0 and 49.3 for the di- and triphenylmethanols. These results show that substitution of a pyridine ring for a benzene ring at a carbonium ion center significantly decreases the thermodynamic stability of the cation as measured by its electrophilicity toward water. Protonation of the pyridine ring must be significant in these ranges of acid concentration to account for these trends. Hence, the destabilization decreases from 2-pyridyl to 4-pyridyl and corresponds to a decrease in the electrostatic repulsion between the sites of positive charge.

Pettit and co-workers (49) have determined the pK_{ROH} values for several thienyl-substituted carbonium ions in sulfuric acid and compared them with the pK_{ROH} values for the isoelectronic homonuclear carbon cations. The equilibria correspond to simple ionization with no concurrent protonation of the heterocyclic moiety. It was found that replacement of a carbon-carbon double bond by a sulfur atom, i.e., in going from a phenyl group to a 2-thienyl group, enhanced the stability of the cation by ca. 4 kcal $mole^{-1}$. Pettit suggests by reference to Hückel molecular orbital calculations that the reason for the increased stability of the thienyl carbonium ions was that the conjugate bases of these systems possessed a much lower π-electron

bonding energy than the carbon systems. Thus, the gain in π-electron bonding energy in going from the conjugate base to the cation was larger for the thienyl systems.

For the isoelectronic series -- pyridyl, phenyl, thienyl -- the trend is toward an increasingly stable carbonium ion. The difference between pyridyl and phenyl is due to these groups not being isoionic in acidic media. The protonation of the pyridyl nitrogen results in an energetically unfavorable di-positive cation; protonation can not occur for the phenyl analogue. The greater stability of the thienyl derivative relative to the phenyl derivative has been rationalized on the basis of differences in π-bonding energies for the conjugate acid and base pairs.

The thiazole nucleus holds a unique position in this isoelectronic series for it is expected to combine the worst features of the pyridyl system with the best features of the thienyl system. The best quantitative comparison would be of the 2-thienyl, 2-pyridyl, and 2-thiazolyl groups attached to an analogous carbonium ion center. The 2-thiazolyl group has both N and S in an α-position to the carbon attached to the central carbon; of course, the α-position in the 2-thienyl group is occupied by S and in the 2-pyridyl group by N. Unfortunately no dilution data were obtained for the 2-pyridyl carbonium ions but only for the 4-pyridyldi(p-tolyl)methyl cation. Comparison with the 2,4-dimethyl-5-thiazolyldi-(p-tolyl)methyl cation may still prove effectual. Table 5 indicates that this latter cation is ca. 4 kcal mole^{-1} more

stable than the 4-pyridyl cation. Subtracting 2 kcal mole^{-1} for the effect of the methyl groups in the 2- and 4-positions leaves the 5-thiazolyl cation 2 kcal mole^{-1} more stable than a 4-pyridyl cation in spite of the fact that one less bond separates the centers of positive charge in the 5-thiazolyl cation. This suggests that, for the thiazolyl carbonium ions, the destabilizing effect of nitrogen protonation on carbonium ion stability is counter-balanced to some extent by the presence of the sulfur atom in the ring; π-bonding differences may be the reason. To obtain an estimate of the magnitude of the destabilization produced by nitrogen protonation, one can compare the $pK_{HROH^{+1}}$ for the 2-thiazolylbis(p-methoxyphenyl)methyl cation with the pK_{ROH} for the 4,4'-dimethoxytriphenylmethyl cation (Tables 5 and 6). The difference of 10 kcal mole^{-1} could amount to a 10^7-fold difference in the relative rates of reactions involving carbonium ion, transition states.

Having estimated the effect of simple protonation on the extent of ionization it would be of interest to consider systems of even higher positive charge. Table 6 lists the pertinent data for a comparison of 4,4'-bis(trimethylamino)-triphenylmethanol and 4,4'-bis(dimethylamino)triphenylmethanol. The former ionizes according to the general scheme

$$ROH^{+2} + H^{+1} = R^{+3} + H_2O \qquad (27)$$

Williams and co-workers (47) have reported the ionization ratios $C_{R^{+3}}/C_{ROH^{+2}}$ in 66-78 percent sulfuric acid. At 72 percent sulfuric acid the log $C_{R^{+3}}/C_{ROH^{+2}} = 0$. If H_R is the

appropriate acidity function for this system, at 72 percent sulfuric acid $pK_{ROH}+2 = -H_R = 12.04$ (8). The free energy of formation of the carbonium ion from its alcohol is 16.37 kcal mole^{-1} at 25^{o}. The pK_{ROH} for the latter compound was determined by Goldacre and Phillips (46) using a series of basic buffers to study the equilibrium

$$ROH = R^{+} + OH^{-} \tag{28}$$

where R^{+} was introduced into solution as the perchlorate salt. The free energy change corresponding to carbonium ion formation is -9.38 kcal mole^{-1}. The difference of ca. 26 kcal mole^{-1} in the formation energies of these two cations shows the effect on ionization of having two sites with full positive charges.

Listed also in Table 6 are the free energies of formation of the 4,4',4"-tris(trimethylamino)triphenylmethanol and 4,4',4"-tris(dimethylamino)triphenylmethanol; the difference of ca. 33 kcal mole^{-1} shows the effect on ionization of having three sites with full positive charges, in addition to the center of varying ionization.

The fact that ionization of these para-dimethylaminophenylmethanols to the carbonium ions occurs at a pH where protonation of the basic amine is negligible suggests a way of directly comparing the effect of a thiazolyl group with a phenyl group. From the previous discussion of heteroaromatic carbonium ions containing S and/or N in the heterocyclic ring it would appear that a thiazole ring and a benzene ring should stabilize a carbonium ion to equivalent

extents if protonation of the thiazole ring were insignificant. The pK_{ROH} determination for 2-thiazolyl-4,4'-bis-(dimethylamino)diphenylmethanol, using the technique of Goldacre and Phillips (46), i.e., at relatively low acid concentration, would alleviate the problem of protonation of the thiazole nitrogen (the pK_a of the thiazolium ion is 2.8) and could be compared with the $pK_{ROH} = -6.90$ for 4,4'-bis(dimethylamino)triphenylmethanol.

Dilution Curves -- Complexed Cations

The complexed cations show dilution curves which closely resemble those of the corresponding free cations. However, interpretation, even on a qualitative basis, is difficult because there are three species, whose concentrations are related by simultaneous equilibria, which may be present at any given time. They are $PdCl_2R_2^{+2}$, $PdCl_2(ROH)R^{+1}$, and $PdCl_2(ROH)_2$. Thus, the absorptivity of the solution is due to both $PdCl_2R_2^{+2}$ and $PdCl_2(ROH)R^{+1}$; the two equilibria present are

$$4H_2O + PdCl_2R_2^{+2} = PdCl_2(ROH)R^{+1} + H_3O^{+1} + 2H_2O = PdCl_2(ROH)_2 + 2H_3O^{+1} \quad (29)$$

There was no evidence of a difference in the λ_{max} for the absorbing species. With the absorptions of the charged species superimposed it is not possible to determine their individual contribution to the absorbance at λ_{max}; only their sum can be observed. This puts severe limitations on any interpretation of the dilution curves in so far as relative stabilities are concerned.

It seemed that by making a certain assumption it might be possible to interpret the dilution curves in a more relevant manner. Namely, it was assumed that $PdCl_2(ROH)R^{+1}$ is substantially more stable than $PdCl_2R_2^{+2}$. Thus, the first part of the dilution curve should represent the equilibrium between $PdCl_2R_2^{+2}$ and $PdCl_2(ROH)R^{+1}$ whereas the latter part of the curve should reflect the equilibrium between $PdCl_2(ROH)R^{+1}$ and $PdCl_2(ROH)_2$. A comparison of the dilution curves so constructed for the free and complexed forms of the carbonium ion reveals that for the less stable phenyl and p-tolyl carbonium ions the first portion of the dilution curve for the complexed cation falls below that of the free cation whereas the curve for the complexed cation crosses that of the free cation and continues to lie above it for the latter portion of the curve. The conclusions which follow naturally from this treatment of the data are:

1. HR^{+2} is more stable with respect to $HROH^{+1}$ than is $PdCl_2R_2^{+2}$ with respect to $PdCl_2(ROH)R^{+1}$.

2. $PdCl_2(ROH)R^{+1}$ is more stable with respect to $PdCl_2(ROH)_2$ than HR^{+2} is with respect to $HROH^{+1}$.

The data used to construct the latter part of the dilution curve for the complex can now be evaluated in terms of $pK_{Pd(ROH)R^{+1}}$, representing the equilibrium between $PdCl_2(ROH)R^{+1}$ and $PdCl_2(ROH)_2$. (Table 7)

The dilution curves for the p-methoxyphenyl carbonium ions -- free and complexed -- do not exhibit the behavior observed for the phenyl and p-tolyl analogues. (The 2-thia-

zolylbis(p-methoxyphenyl)methyl cation is an exception.) That is, the dilution curves for the complexed cations do not initially fall below those of the free cations but rather remain above them throughout. This makes our previously stated assumption (that $PdCl_2(ROH)R^{+1}$ is considerably more stable than $PdCl_2R_2^{+2}$) questionable for the p-methoxyphenyl cations and denies us the advantage of interpreting different segments of the dilution curves in terms of species for which we know the concentration.

Referring to Tables 5 and 7 it is apparent that whereas the variation of the values for $dH_R/d\log Q$ and $pK_{Pd(ROH)R^{+1}}$ are similar to those observed for the free cations, the remainder of the complexed cations exhibit a wider variation of these values. This is especially true for the complexed 4,5-dimethyl-2-thiazolyldi(p-tolyl)-methyl cation. The variation is most likely due to a weakness in the basic assumption. That is, whereas it may be true that the latter part of the dilution curves does reflect the stated equilibrium there is also a likely contribution to the absorbance from $PdCl_2R_2^{+2}$, i.e., $PdCl_2(ROH)R^{+1}$ may not be substantially more stable than $PdCl_2R_2^{+2}$.

Comparison of the free energies of formation for the free and complexed form of the cation suggests that complexation does stabilize the cation. This extra stability amounts to as much as 3 kcal mole^{-1} for the 2,4-dimethyl-5-thiazolyldiphenylmethyl cation and to as little as 0.5 kcal mole^{-1} for both the 2-thiazolyldi(p-tolyl)methyl and 2-thia-

zolylbis(*p*-methoxyphenyl)methyl cations.

The effect of varying the halogen coordinated to palladium was determined for the 4-methyl-2-thiazolyldi(*p*-tolyl)-methyl cation. The results in Tables 7 and 8 demonstrate that a change of the halogen from chloride to bromide stabilizes the cation by *ca*. 1 kcal mole^{-1}. This finding is consistent with stabilization of the cation through a back-bonding mechanism from metal to ligand. This type of resonance interaction is transmitted by either partial or complete overlapping of the π-molecular orbitals of the ligands with the filled *d* orbitals on the metal atom. On this basis the increase in stability is expected considering that bromide lies higher in the Nephelaxetic Series than chloride and should tend to be a better π-electron donor. In the square-planar arrangement of the ligands around the central metal atom the halogen atom lies *cis* to the coordinated cation and for this reason the effect of their π-interaction is not as large as if they were located *trans* to each other.

The increase in stability which arises upon complexation may be viewed simply on the basis of charge effects. In the free cation protonation of the thiazole ring nitrogen contributes to an energetically less favorable di-positive cation. In effect, coordination to palladium reduces the overall charge of the system with nitrogen bound to a neutral moiety. In comparing the relative stabilities of HR^{+2} and $PdCl_2(ROH)R^{+1}$, the decrease in charge by one unit may well be the main factor involved. This consideration complicates our understanding of the role of the metal atom as far as

stabilizing or destabilizing the carbonium ion is concerned and tends to deemphasize the importance of back-bonding as a mechanism for stabilizing the carbonium ion. The increase in stability on going from chloride to bromide as the other ligand may then be a direct consequence of increasing the overall size of the system.

An elucidation of the exact nature and extent of the interaction between coordinated cation and ligands and metal atom will follow only after a more extensive investigation of these model systems. A logical extension to the present work would be to prepare the 1:1 complexes of the thiazolylmethanols and palladium(II) and investigate the effect of different ligands on the stability of the complexed cations. It might also prove enlightening to coordinate to the thiazole ring nitrogen a neutral moiety such as BF_3. With back-bonding to the cation eliminated, the effect of σ-bond formation could be begun to be evaluated. This would place in better perspective the relative importance of protonation, σ-bond formation, and back-bonding on carbonium ion stability.

PMR and EPR Spectra

The pmr spectrum of the methyl iodide salt of 2,4-dimethyl-5-thiazolyldi(p-tolyl)methanol in deuterochloroform shows the effect of a positive charge on the chemical shifts of the protons. As expected the resonances due to the methyl groups on the thiazole ring are displaced downfield from their position in the parent methanol. (Table 9) The A_2B_2 resonance pattern of the benzene ring protons shows a small downfield shift while the p-tolyl methyl resonance has not shifted. These findings suggest that the positive charge is localized primarily on the thiazole ring with the small benzene ring proton shifts due to a weak inductive effect.

The pmr spectra of the carbonium ions exhibit the downfield shifts expected on the basis of charge effects. Compared with their resonance position in the parent methanols the phenyl protons are shifted downfield by ca. 30 Hz. The p-methoxy proton resonances show downfield shifts of similar magnitude. These shifts support the contention that the positive charge developed at the carbonium ion center is spread out over the benzene rings.

The resonances attributable to the thiazole ring protons were not observed in perchloric acid due to masking by the broad solvent peak. The resonances due to the methyl groups at the 4- and/or 5-positions on the thiazole ring showed the downfield shifts anticipated on the basis of protonation and carbonium ion formation.

However, it is really difficult to interpret chemical shifts on the basis of charge effects without a thorough investigation of the effect of solvent changes and protonation of the thiazole ring in the absence of carbonium ion formation. The data for the methyl iodide salt proved to be revealing but were limited in scope. For this reason it is impossible to establish any trends in the chemical shifts which might be used to determine the relative stabilities of the carbonium ions. The preparation of either the the methyl iodide or hydrochloride salts of the remaining thiazolylmethanols would serve to bridge the gap in our knowledge of these systems.

The spontaneous generation of free radical species at concentrations of carbonium ion appropriate for pmr spectroscopy makes it impossible to obtain the pmr spectra for any of the cations involved. While the pmr characterization would have provided additional insight into the structure and charge distribution in these cations it would have only served to supplement the visible spectral data. For this reason these free radical species have provided an interesting although perplexing sidelight but have not seriously compromised our fundamental approach to establishing relative stabilities, i.e., at the concentration of carbonium ion present during the $pK_{HROH}+1$ determinations no epr signal was observed.

SUMMARY

The reaction between the appropriate thiazolyllithium reagent and either benzophenone, 4,4'dimethylbenzophenone, or 4,4'dimethoxybenzophenone led to the preparation of the triarylmethanols described. Yields greater than 50 percent can be obtained for these reactions. The triarylmethanols served as the precursors to the carbonium ions which were formed in perchloric acid and characterized by their intense colors (the molar absorptivities were <u>ca</u>. 10^4). The fact that these carbonium ions can only be generated at an acid strength greater than that required for the trityl cation suggests that protonation of the thiazole ring nitrogen contributes to their relative instability. That the methyl cations were protonated in strong acid was inferred from a comparison of the properties of the 2,4-dimethyl-5-thiazolyldi(<u>p</u>-tolyl)methyl cation with its N-methyl iodide analogue.

The H_R acidity function was employed to extrapolate equilibrium data obtained at high acid strengths to their standard state in aqueous medium. Use was made of the striking difference in visible absorption spectra for the species HR^{+2} and $HROH^{+1}$ (HR^{+2} has at least one intense absorption in the visible region whereas $HROH^{+1}$ has none) to determine the ratio $C_{HR^{+2}}/C_{HROH^{+1}}$ used to calculate

$pK_{HROH^{+1}}$. The experimental technique employed was to obtain the dilution curve characteristic of the equilibrium between HR^{+2} and $HROH^{+1}$; points chosen in the vicinity of the midpoint were used to calculate $pK_{HROH^{+1}}$ values having the least scatter. The appropriateness of the H_R acidity function was demonstrated and enabled the interpretation of $pK_{HROH^{+1}}$ as the correct thermodynamic measure of carbonium ion stability.

The carbonium ion stability within a series was observed to increase as the para-substituent on the phenyl ring changed from -H, to $-CH_3$, to $-OCH_3$, in keeping with established resonance effects in fully conjugated carbonium ion systems. The substitution of methyl groups at the 5- and/or 4-position on the thiazole ring leads to an increase in stability of ca. 1 kcal $mole^{-1}$ per methyl group substituted. The 2,4-dimethyl-5-thiazolyl-substituted carbonium ions are the most stable among those with identical phenyl substituents, a fact attributed to the greater separation between the centers of positive charge (the carbonium ion center and the protonated thiazole ringnitrogen). The fact remains, however, that due to protonation only the 2,4-dimethyl-5-thiazolylbis(p-methoxyphenyl)methyl cation is more stable than the unsubstituted triphenylmethyl cation.

The preparation of the 1:2 dichloropalladium(II) complexes of the thiazolylmethanols was accomplished by reacting the ligand with the tetrachloropalladate(II) ion in either methanol or acetone solutions. Each of these

complexes forms the analogous carbonium ion species in concentrated perchloric acid. Dilution curves were obtained for these complexed carbonium ions. An interpretation of the dilution curves was fashioned on the assumption that the thermodynamic stability of the species $PdCl_2(ROH)R^{+1}$ is significantly greater than that of the species $PdCl_2R_2^{+2}$. Thus, the latter part of the dilution curve was viewed in terms of an equilibrium between $PdCl_2(ROH)R^{+1}$ and $PdCl_2(ROH)_2$. The $pK_{Pd(ROH)_2}$ was subsequently calculated. A comparison with the $pK_{HROH^{+1}}$ for the free cation indicates that complexation has stabilized the carbonium ion. This increase in stability ranges from 0.5 kcal mole^{-1} for the 2-thiazolylbis(p-methoxyphenyl)methyl cation to 3 kcal mole^{-1} for the 2,4-dimethyl-5-thiazolyldiphenylmethyl cation. No trends were evident, based on the few complexed cations for which $pK_{Pd(ROH)_2}$ values were calculated.

A change from chloride to bromide bonded to palladium led to an increase in the stability of the 4-methyl-2-thiazolyldi(p-tolyl)methyl cation. This suggested that a back-bonding mechanism was operative whereby the charge at the carbonium ion center was reduced as the result of overlap of filled d orbitals on the metal with ligand p-π orbitals of the appropriate symmetry.

It appears, however, that the greater stability of the complexed carbonium ion can be more realistically attributed to a reduction of the overall charge on the system with nitrogen bound to a neutral moiety; protonation of the free cation contributes to an energetically less favorable di-positive cation.

APPENDICES

1. Derivation of Volume Changes Upon Dilution

Before titration data for the carbonium ions could be evaluated it was necessary to determine the volume changes of the perchloric acid solution upon the dropwise addition of water; literature data were available for this (Table 11 and Figure 46). The following relationships were employed:

$$\text{wt. \% } HClO_4 = \frac{g_{HClO_4}}{\text{sp. gr.(g/ml) x volume(ml)}} \times 100 \qquad (30)$$

$$\text{volume(ml)} = \frac{g_{HClO_4}}{\text{sp. gr.(g/ml) x wt. \% } HClO_4} \times 100 \qquad (31)$$

The specific gravity of the perchloric acid solution prior to dilution was determined by using a Westphal balance and corresponded to 69.0 percent perchloric acid (sp. gr. = 1.651). For an initial volume of 2 ml the solution contained 2.278 g perchloric acid. The volume changes upon dilution were calculated from a knowledge of the specific gravity and weight percent perchloric acid.

$$\text{wt. \% } HClO_4 = \frac{g_{HClO_4}}{g_{HClO_4} + g_{H_2O}} \times 100 \qquad (32)$$

for example,

$$69.00 = \frac{2.278}{2.278 + 1.024} \times 100 \tag{33}$$

The calculated decrease in weight percent perchloric acid upon dilution comes from the expression,

$$\text{wt. \% } HClO_4 = \frac{2.278}{3.302 + 0.0480n} \times 100 \tag{34}$$

where n = number of drops of water added having an average weight of 0.0480 g/drop. The stepwise addition of 30 drops of water gives the changes in weight percent perchloric acid indicated in Table 12.

The changes in specific gravity were determined using the data given in Table 11; a graphical representation of the specific gravity--weight percent perchloric acid relationship appears in Figure 46. A straight line was drawn between the points for 50 and 70 percent perchloric acid and the equation for that line was obtained by solving two simultaneous equations.

$$\text{sp. gr.} = 0.0132(\text{wt. \% } HClO_4) + 0.7395 \tag{35}$$

Using the values of weight percent perchloric acid given in Table 12 the corresponding changes in specific gravity were calculated. Volume changes were calculated using equation (31); the <u>dilution fraction</u> corresponds to 2.000 divided by the volume.

The evaluation of titration data obtained using 46 percent perchloric acid was made with the assumption that the volumes of perchloric acid solution and water were additive. The weight percent perchloric acid was calculated from equation (34) and was used in conjunction with the weight percent--H_R relationship presented in Table 3.

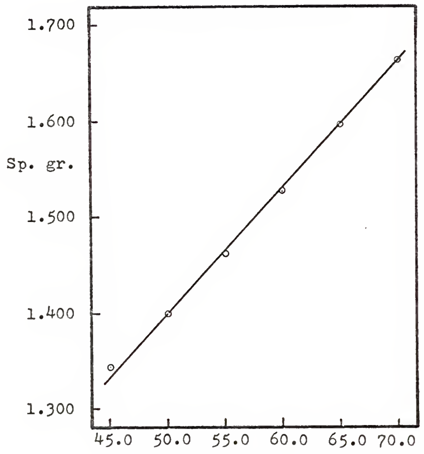


Fig. 46.--Specific Gravity of Aqueous Perchloric Acid Solutions at 25°

TABLE 11[a]

SPECIFIC GRAVITY OF AQUEOUS PERCHLORIC ACID SOLUTIONS AT 25°

Weight % $HClO_4$	Specific Gravity
70.0	1.664
65.0	1.596
60.0	1.527
55.0	1.462
50.0	1.400
45.0	1.343

[a]Brickwedde (44).

TABLE 12

VOLUME CHANGES OF PERCHLORIC ACID SOLUTION UPON DILUTION

n	Weight % $HClO_4$	Sp. Gr. (g/ml)	v(ml)	Dilution Fraction (2.000/v)
0	69.00	1.651	2.000	1.000
1	68.01	1.638	2.045	0.978
2	67.05	1.625	2.090	0.957
3	66.11	1.613	2.136	0.936
4	65.20	1.601	2.181	0.917
5	64.32	1.589	2.228	0.898
6	63.46	1.578	2.275	0.879
7	62.62	1.567	2.322	0.861
8	61.81	1.556	2.367	0.845
9	61.01	1.545	2.415	0.828
10	60.24	1.535	2.462	0.812
11	59.48	1.525	2.511	0.796
12	58.75	1.516	2.556	0.782
13	58.03	1.506	2.606	0.767
14	57.33	1.497	2.655	0.753
15	56.64	1.488	2.702	0.740
16	55.98	1.479	2.751	0.727
17	55.32	1.470	2.801	0.714
18	54.69	1.462	2.847	0.702
19	54.06	1.454	2.898	0.690
20	53.45	1.446	2.946	0.679
21	52.86	1.438	2.997	0.667
22	52.28	1.430	3.045	0.657
23	51.71	1.423	3.095	0.646
24	51.15	1.415	3.146	0.636
25	50.60	1.408	3.199	0.625
26	50.07	1.401	3.249	0.616
27	49.55	1.394	3.296	0.606
28	49.04	1.387	3.350	0.597
29	48.53	1.381	3.400	0.588
30	48.04	1.374	3.451	0.580

2. Structures of thiazolylbis(*p*-methoxyphenyl)methanols

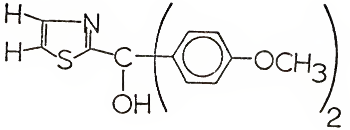


Fig. 47.--2-thiazolylbis(p-methoxyphenyl)methanol

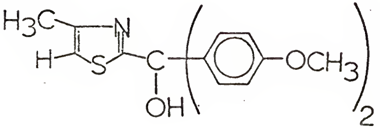


Fig. 48.--4-methyl-2-thiazolylbis(p-methoxyphenyl)methanol

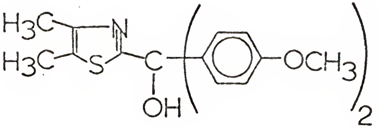


Fig. 49.--4,5-dimethyl-2-thiazolylbis(p-methoxyphenyl)methanol

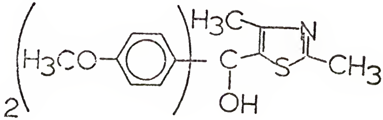


Fig. 50.--2,4-dimethyl-5-thiazolylbis(p-methoxyphenyl)methanol

BIBLIOGRAPHY

1. J. L. Franklin in "Carbonium Ions," Vol. 1, G. A. Olah and P. von R. Schleyer, Eds., Interscience, New York, N. Y., 1968, p 94.

2. C. D. Nenitzescu in "Carbonium Ions," Vol. 1, G. A. Olah and P. von R. Schleyer, Eds., Interscience, New York, N. Y., 1968, p 9.

3. G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, J. Amer. Chem. Soc., 86, 1360 (1964).

4. D. Bethell and V. Gold, "Carbonium Ions An Introduction," Academic Press, New York, N. Y., 1967, pp 49-50..

5. H. A. Skinner in "Cationic Polymerization and Related Complexes," P. H. Plesch, Ed., W. Heffer, Cambridge, 1953, p 28.

6. G. A. Olah, A. Pavlath, and J. A. Olah, J. Amer. Chem. Soc., 80, 6540 (1958).

7. A. G. Evans, A. Bentley, and J. Halpern, Trans. Faraday Soc., 47, 711 (1951)

8. N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, J. Amer. Chem. Soc., 77, 3044 (1955).

9. L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter IX.

10. E. D. Jensen and R. W. Taft, J. Amer. Chem. Soc., 86, 116 (1964).

11. A. K. Colter, I. I. Schuster, and R. J. Kurland, J. Amer. Chem. Soc., 87, 2278 (1965).

12. R. Dehl, W. R. Vaughn, and R. S. Berry, J. Org. Chem., 24, 1616 (1959).

13. R. B. Moodie, T. M. Connor, and R. Stewart, Can. J. Chem., 37, 1402 (1959).

14. T. Schaefer and W. G. Schneider, Can. J. Chem., 41, 966 (1963).

15. G. Fraenkel and D. G. Farnum in "Carbonium Ions," Vol. 1, G. A. Olah and P. von R. Schleyer, Eds., Interscience, New York, N. Y., 1968, p 242.

16. D. G. Farnum, J. Amer. Chem. Soc., 86, 934 (1964).

17. R. W. Taft and L. D. McKeever, J. Amer. Chem. Soc., 87, 2489 (1965).

18. H. J. Dauben and L. R. Honnen, J. Amer. Chem. Soc., 80, 5570 (1958).

19. A. Davison, M. L. H. Green, and G. Wilkinson, J. Chem. Soc., 3171 (1961).

20. E. O. Fisher and R. D. Fisher, Angew. Chem., 72, 919 (1960).

21. H. J. Dauben and D. J. Bertelli, J. Amer. Chem. Soc., 83, 497 (1961).

22. G. W. Schrauzer, J. Amer. Chem. Soc., 83, 2966 (1961).

23. G. F. Emerson and R. Pettit, J. Amer. Chem. Soc., 84, 4591 (1962).

24. J. E. Mahler and R. Pettit, J. Amer.Chem. Soc., 84, 1511 (1962).

25. N. A. Clinton and C. P. Lillya, J. Amer. Chem. Soc., 92, 3065 (1970).

26. J. H. Richards and E. A. Hill, J. Amer. Chem. Soc., 83, 3840 (1961).

27. M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards, Tetrahedron Lett., 15, 1695 (1966).

28. S. Winstein and E. Grunwald, J. Amer. Chem. Soc., 70, 828 (1948).

29. R. Pettit, J. D. Fitzpatrick, and L. Watts, Tetrahedron Lett., 12, 1299 (1966).

30. J. C. Ware and T. G. Traylor, Tetrahedron Lett., 18, 1295 (1965).

31. J. Feinberg and M. Rosenblum, J. Amer. Chem. Soc., 91, 4324 (1969).

32. M. Hisatome and K. Yamakawa, Tetrahedron, 27, 2101 (1971).

33. M. Rosenblum and F. W. Abbate in "Werner Centennial," Advances in Chemistry Series, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1967, p 536.

34. E. A. Hill and R. Wiesner, J. Amer. Chem. Soc., 91 509 (1969).

35. M. D. Raush, D. F. Hunt, and C. P. Lillya, J. Amer. Chem. Soc., 90, 2561 (1968).

36. T. W. Richardson, Doctoral Dissertation, University of Florida, 1971, p 10.

37. R. P. Kurkjy and E. V. Brown, J. Amer. Chem. Soc., 74, 6260 (1952).

38. M. N. Hughes and K. J. Rutt, Inorg. Chem., 10, 414 (1971).

39. J. A. Weaver, P. Hambright, P. T. Talbert, E. Kang, and A. N. Thorpe, Inorg. Chem., 9, 268 (1970).

40. H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, J. Amer. Chem. Soc., 71, 1499 (1949).

41. K. Ganapathi and A. Venkataraman, Proc. Indian Acad. Sci., 22A, 343.362 (1945).

42. R. P. Kurkjy and E. V. Brown, J. Amer. Chem. Soc., 74, 5778 (1952).

43. B. M. Mikhailov and V. P. Bronovitskaya, Zh. Obshch. Khim., 27, 726 (1957).

44. L. H. Brickwedde, J. Res. Nat. Bur. Stand., 42A, 309 (1949).

45. N. C. Deno, H. E. Berkheimer, W. L. Evans, and H. J. Peterson, J. Amer. Chem. Soc., 81, 2344 (1959).

46. R. J. Goldacre and J. H. Phillips, J. Chem. Soc., 1724 (1949).

47. G. Williams, M. A. Murray, and A. M. Lowen, J. Chem. Soc., 3318 (1950).

48. G. V. Epple, V. P. Odintsova, and S. G. Entelis, Izv. Akad. Nauk SSSR,Otd. Khim. Nauk, 1365 (1962).

49. R. Pettit, R. G. Turnbo, and D. L. Sullivan, J. Amer. Chem. Soc., 86, 5630 (1964).

50. J. Metzger and J. Beraud, Bull. Soc. Chim. Fr., 2072 (1962).

51. J. Metzger and J. Crousier, Bull. Soc. Chim. Fr., 4134 (1967).

52. C. H. Rochester in "Acidity Functions," Organic Chemistry Monograph Series, Vol. 17, A. T. Blomquist, Ed., Academic Press, New York, N. Y., 1970, p 77.

53. E. M. Arnett and R. D. Bushick, J. Amer. Chem. Soc., 86, 1564 (1964).

54. H. A. Smith and C. W. Holley, J. Amer. Chem. Soc., 80, 3714 (1958).

BIOGRAPHICAL SKETCH

Peter William Wentz was born December 26, 1944 in Brooklyn, New York. He graduated from Watkins Glen Central School in June, 1962. He attended Ithaca College where he was listed in Who's Who Among Students in American Colleges and Universities and graduated, cum laude in June, 1966, with a Bachelor of Arts degree in Chemistry.

He enrolled in Graduate School at the University of Florida in September 1966 where, until the present time, he has pursued his work toward the degree of Doctor of Philosophy. During those years he held graduate teaching assistantships, graduate research assistantships and a N.D.E.A. Title IV Fellowship. After these assistantships ended he held a post-doctoral position at the University of Florida Medical Center.

Mr. Wentz married the former Margaret Mary Geiger in May, 1968, and they have one child, Kristina Marie.

He is a member of the American Chemical Society.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

R. Carl Stoufer

R. Carl Stoufer, Chairman
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Merle A. Battiste

Merle A. Battiste
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

GERyschkewitsch

George E. Ryschkewitsch
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

W. Weltner, Jr.

W. Weltner, Jr.
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

J. Kenneth Watson

J. Kenneth Watson
Associate Professor of Electrical Engineering

This dissertation was submitted to the Department of Chemistry in the College of Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

June, 1972

Dean, Graduate School